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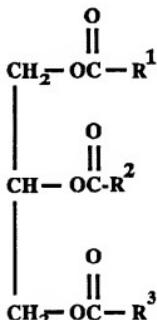
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(54) Pour point depressant treated fatty acid esters as biodegradable, combustion engine fuels.

(55) A composition is described that comprises  
(A) esters from the transesterification of at least one animal fat or vegetable oil triglyceride of the formula



with an alcohol R<sup>4</sup>OH wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are aliphatic groups containing from about 6 to about 24 carbon atoms and R<sup>4</sup> is an aliphatic group containing from 1 to about 10 carbon atoms ; and

(B) a pour point depressant.

In addition to components (A) and (B), the composition may also contain an additive (C) and/or (D) a normally liquid fuel.

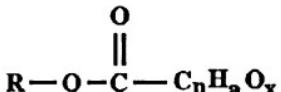
The present invention relates to natural oils such as animal oils and vegetable oils that are transesterified and contain at least one pour point depressant. In addition to pour point depressants, the transesterified natural oil may also contain additional additives as well as a normally liquid fuel.

5      BACKGROUND OF THE INVENTION

Successful use of esters of transesterified natural oils as environmentally friendly, that is biodegradable, base fluids in industrial applications and also as a fuel additive when mixed with normally liquid fuels, is contingent upon improving their low temperature viscometries. For example, a methyl ester obtained from the transesterification of 10 rapeseed oil, has utility as an environmentally friendly diesel fuel. However, this methyl ester has a pour point of -12°C and solidifies at 13.6°C which results in clogged filters and engine failure. In order to take advantage of the biodegradability of transesterified esters of natural oils, it becomes necessary to lower the pour point.

U.S. Patent No. 2,243,198 (Dietrich, May 27, 1941) relates to non-viscous normally liquid hydrocarbon oils and more particularly to the production of fuel oils having improved flow characteristics under low temperature conditions. The flow characteristics of fuel oil is improved by the addition of a hydrogenated castor oil derivative to a non-viscous normally liquid hydrocarbon oil. Hydrogenated castor oil derivative is defined as the product obtained by reacting hydrogenated castor oil either with its own hydroxyl group or with another organic compound selected from the classes of alcohols, aldehydes, acids, isocyanates and isothiocyanates.

U.S. Patent No. 4,364,743 (Erner, December 21, 1982) relates to a fuel source for oil burning devices which 20 is a fuel in and of itself or can be mixed with petroleum middle distillates. Fatty acids of the formula



can provide such a fuel wherein

30      (a) R is (1) an alkyl radical having from 1 to 12 carbon atoms, (2) alkoxy alkyl wherein the alkoxy portion has from 1 to 4 carbon atoms and the alkyl portion is ethyl or propyl, (3) cyclopentyl or cyclohexyl and (4) hydroxy ethyl and hydroxy propyl;  
 (b) n = 11-22;  
 (c) a =  $2_{n+1}$ ,  $2_{n-1}$ ,  $2_{n-3}$ ,  $2_{n-5}$ , or  $2_{n-7}$ ; and  
 (d) x is 0 or 1.

35      U.S. Patent No. 4,575,382 (Sweeney et al, March 11, 1986) relates to a vegetable oil containing middle distillate fuel characterized by an improved thermal stability. The vegetable oils which may be used include soybean oil, peanut oil and sunflower seed oil.

U.S. Patent 4,695,411 (Stern et al, September 22, 1987) relates to a process for manufacturing a major 40 portion of ethyl esters usable as gas oil substitute motor fuel by transesterification of an animal or vegetable oil optionally containing free acids.

U.S. Patent 5,160,506 (Schur et al, November 3, 1992) relates to a liquid fuel mixture, comprising a C<sub>3</sub> and/or at least a C<sub>4</sub>-alkane, at least one oil component and optionally at least one additive, a process for its preparation and its use for two-stroke engines.

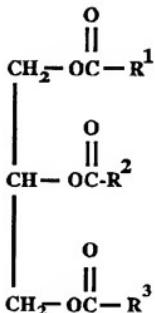
45      SUMMARY OF THE INVENTION

A composition is disclosed which comprises

(A) esters from the transesterification of at least one animal fat or vegetable oil triglyceride of the formula

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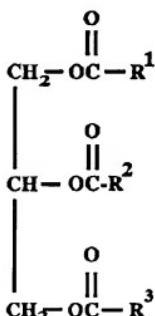
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- 20 with an alcohol  $\text{R}^4\text{OH}$  wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are aliphatic groups containing from about 6 to about 24 carbon atoms and  $\text{R}^4$  is an aliphatic group containing from 1 to about 10 carbon atoms; and  
(B) a pour point depressant.  
In addition to components (A) and (B), the composition may also contain an additive (C) and/or (D) a normally liquid fuel.
- 25 Various preferred features and embodiments of the invention are described below by way of non-limiting illustration.

(A) The Transesterified Esters

- 30 In practicing this invention, a natural oil comprising animal fat or vegetable oils is reacted with an alcohol to obtain the transesterified esters. These natural oils include triglycerides of the formula



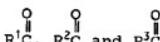
- 35 wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are aliphatic hydrocarbyl groups containing from about 6 to about 24 carbon atoms. The term "hydrocarbyl group" as used herein and throughout this specification and claims denotes a radical having a carbon atom directly attached to the remainder of the molecule. The aliphatic hydrocarbyl groups include the following:  
40 (1) Aliphatic hydrocarbon groups; that is, alkyl groups such as heptyl, nonyl, undecyl, tridecyl, heptadecyl; alkanyl groups containing a single double bond such as heptenyl, nonenyl, undecenyl, tridecenyl, hepta-decenyl, heneicosenyl; alkenyl groups containing 2 or 3 double bonds such as 8,11-heptadecadienyl and 55 8,11,14-heptadecatrienyl. All isomers of these are included, but straight chain groups are preferred.

(2) Substituted aliphatic hydrocarbon groups; that is groups containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents; examples are hydroxy, carbalkoxy, (especially lower carbalkoxy) and alkoxy (especially lower alkoxy), the term, "lower" denoting groups containing not more than 7 carbon atoms.

(3) Hetero groups; that is, groups which, while having predominantly aliphatic hydrocarbon character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of aliphatic carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, oxygen, nitrogen and sulfur.

10 Animal fats having utility include beef tallow oil and menhaden oil. Useful vegetable oils include sunflower oil, cottonseed oil, safflower oil, corn oil, soybean oil, rapeseed oil, meadowfoam oil or any of the previously mentioned vegetable oils that are genetically modified such that the monounsaturated content is greater than the normal value. For example, a synthetic triglyceride prepared by reacting one mole of glycerol with three moles of oleic has an oleic acid content of 100% and consequently a monounsaturated content of 100%. Normal sunflower oil has an oleic acid content of 25-30%. By genetically modifying the seeds of sunflowers, a sunflower oil can be obtained wherein the oleic acid content is from about 60% up to about 90%.

15 It is preferred that the monounsaturated character be derived from an oleyl radical, i.e.,



is the residue of oleic acid. The preferred triglyceride oils are high oleic (at least 60 percent) acid triglyceride oils. Typical high oleic vegetable oils employed within the instant invention include high oleic safflower oil, 25 high oleic corn oil, high oleic rapeseed oil, high oleic sunflower oil, high oleic soybean oil, high oleic cottonseed oil and high oleic palm olein. A preferred high oleic vegetable oil is high oleic sunflower oil obtained from Helianthus sp. This product is available from SVO Enterprises, Eastlake, Ohio as Sunyl® high oleic sunflower oil. Sunyl 80 is a high oleic triglyceride wherein the acid moieties comprise 80 percent oleic acid. Another preferred high oleic vegetable oil is high oleic rapeseed oil obtained from Brassica campestris or Brassica napus, also available from SVO Enterprises as RS® high oleic rapeseed oil. RS80 signifies a rapeseed oil wherein the acid moieties comprise 80 percent oleic acid.

30 Alcohol utilized in forming the transesterified esters are of the formula  $\text{R}^4\text{OH}$  wherein  $\text{R}^4$  is an aliphatic group that contains from 1 to about 24 carbon atoms. The  $\text{R}^4$  may be straight chained or branched chain, saturated or unsaturated. An illustrative but non exhaustive list of alcohols are: methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol and the isomeric butyl, pentyl, hexyl, heptyl, octyl, nonyl dodecyl, pentadecyl and octadecyl alcohols. Preferably the alcohol is methyl alcohol.

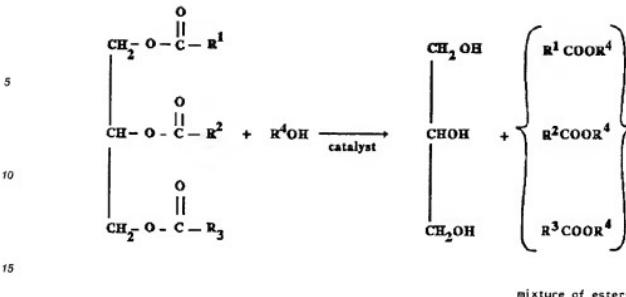
35 The transesterification generally occurs by mixing at least 3 moles of  $\text{R}^4\text{OH}$  per 1 mole of triglyceride. A catalyst, when employed, comprises alkali or alkaline earth metal alkoxides containing from 1 up to 6 carbon atoms. Preferred catalysts are sodium or potassium methoxide, calcium or magnesium methoxide, the ethoxides of sodium, potassium, calcium or magnesium and the isomeric propoxides of sodium, potassium, calcium or magnesium. The most preferred catalyst is sodium methoxide.

40 The transesterification conveniently occurs at a temperature of from ambient up to the decomposition temperature of any reactant or product. Usually the upper temperature limit is not more than 150°C and preferably not more than 120°C. In the transesterification mixed esters are obtained according to the following reaction:

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Transesterification is an equilibrium reaction. To shift the equilibrium to the right it is usually necessary to use either a large excess of alcohol, or else remove glycerol as it is formed. When using an excess of alcohol, once the transesterification reaction is complete the excess alcohol is removed by distillation.

The following non-limiting examples are illustrative of the preparation of the transesterified product of the present invention. Unless otherwise indicated, all parts and percentages are by weight.

#### Example A-1

Charged to a 12 liter 4 neck flask is 7056 parts (8 moles) high oleic rapeseed oil, 1280 parts (40 moles) absolute methyl alcohol and 70.5 parts (1.30 moles) sodium methoxide. The contents are heated to a reflux temperature of 73°C and held at this temperature for 3 hours and 76 parts (0.65 moles) of 85% phosphoric acid is added dropwise in 0.4 hours to neutralize the catalyst. Excess methyl alcohol is then removed by heating to 100°C with nitrogen blowing at 0.2 cubic feet per hour and later to a vacuum of 30 millimeters of mercury. The contents are filtered to give 6952 parts of the transesterified methyl ester of high oleic rapeseed oil.

#### Example A-2

The procedure of Example A-1 is essentially followed except that the high oleic rapeseed oil is replaced with high oleic sunflower oil to give the transesterified methyl ester of high oleic sunflower oil.

#### Example A-3

Charged to a 5 liter 4 neck flask is 759 parts (12.5 moles) isopropyl alcohol. While at room temperature, 5.75 parts (0.25 moles) elemental sodium is slowly added. When all the sodium is reacted, added is 2205 (25 moles) high oleic sunflower oil. The contents are heated to 85°C and held for 4 hours followed by neutralization of the catalyst with 9.67 parts (0.083 moles) of 85% phosphoric acid. The contents are stripped to 120°C at 27 millimeters of mercury to give 2350 parts of the transesterified isopropyl ester of high oleic sunflower oil.

#### Example A-4

The procedure of Example A-3 is essentially followed except that the catalyst is made by reacting 690 parts (15 moles) absolute ethyl alcohol with 6.9 parts (0.3 moles) sodium metal. The product obtained is the transesterified ethyl ester of high oleic sunflower oil.

#### Example A-5

The procedure of Example A-3 is essentially followed except that the catalyst is made by reacting 910 parts (15 moles) n-propyl alcohol with 6.9 parts (0.3 moles) sodium metal. The product obtained is the transesterified n-propyl ester of high oleic sunflower oil.

Example A-6

The procedure of Example A-3 is essentially followed except that the catalyst is made by reacting 1114.5 parts (15 moles) n-butyl alcohol with 6.9 parts (0.3 moles) sodium metal. The product obtained is the trans-esterified n-butyl ester of high oleic sunflower oil.

Example A-7

The procedure of Example A-3 is essentially followed except that the catalyst is made by reacting 1300 (12.5 moles) n-hexyl alcohol with 5.75 parts (0.25 moles) sodium metal. The product obtained is the trans-esterified n-hexyl ester of high oleic sunflower oil.

Example A-8

Utilizing the catalyst as prepared in Example A-3, safflower oil is transesterified with isopropyl alcohol to obtain transesterified isopropyl esters of safflower oil.

Example A-9

Utilizing the catalyst as prepared in Example A-4, cottonseed oil is transesterified with ethyl alcohol to obtain transesterified ethyl esters of cottonseed oil.

Example A-10

Utilizing the catalyst as prepared in Example A-6, corn oil is transesterified with n-butyl alcohol to obtain transesterified n-butyl esters of corn oil.

Example A-11

The procedure of Example A-9 is essentially followed except that beef tallow oil is utilized instead of cottonseed oil. The product obtained is the transesterified ethyl ester of beef tallow oil.

Example A-12

The procedure of Example A-10 is essentially followed except that menhaden oil is utilized instead of corn oil. The product obtained is the transesterified n-butyl ester of menhaden oil.

Example A-13

The procedure of Example A-1 is essentially followed except that rapeseed oil is utilized instead of high oleic rapeseed oil. The product obtained is the transesterified methyl ester of rapeseed oil.

Example A-14

The procedure of Example A-1 is essentially followed except that soybean oil is utilized instead of high oleic rapeseed oil. The product obtained is the transesterified methyl ester of soybean oil.

(B) The Pour Point Depressant

A drawback of using transesterified esters is in the difficulty with congelation of the transesterified esters at low temperatures (less than -10°C). This difficulty arises from a natural stiffening at low temperatures of the transesterified esters analogous to the stiffening of honey or molasses at a reduced temperature. To maintain the "pour" or "flow" of the transesterified esters, a pour point depressant is added to the oil.

Preferred, pour point depressants (PPD) having utility in this invention are carboxy containing interpolymers in which many of the carboxy groups are esterified and the remaining carboxy groups, if any, are neutralized by reaction with amino compounds; acrylate polymers, nitrogen containing acrylate polymers and methylene linked aromatic compounds.

Carboxy-Containing Interpolymers

This PPD is an ester of a carboxy-containing interpolymer, said interpolymer having a reduced specific viscosity of from about 0.05 to about 2, said ester being substantially free of titratable acidity, i.e., at least 90% esterification, and being characterized by the presence within its polymeric structure of pendant polar groups: (A) a relatively high molecular weight carboxylic ester group having at least 8 aliphatic carbon atoms in the ester radical, (B) a relatively low molecular weight carboxylic ester group having no more than 7 aliphatic carbon atoms in the ester radical, and optionally (C) a carbonyl-polyamino group derived from a polyamino compound having one primary or secondary amino group, wherein the molar ratio of (A):(B) is (1-20):1, preferably (1-10):1 and wherein the molar ratio of (A) : (B) : (C) is (50-100);(5-50);(0.1-15)

An essential element of this ester is that the ester is a mixed ester, i.e., one in which there is the combined presence of both a high molecular weight ester group and a low molecular weight ester group, particularly in the ratio as stated above. Such combined presence is critical to the viscosity properties of the mixed ester, both from the standpoint of its viscosity modifying characteristics and from the standpoint of its thickening effect upon lubricating compositions in which it is used as an additive.

In reference to the size of the ester groups, it is pointed out that an ester radical is represented by the formula -C(O) (OR)

and that the number of carbon atoms in an ester radical is the combined total of the carbon atoms of the carbonyl group and the carbon atoms of the ester group i.e., the (OR) group.

An optional element of this ester is the presence of a polyamino group derived from a particular amino compound, i.e., one in which there is one primary or secondary amino group and at least one mono-functional amino group. Such polyamino groups, when present in this mixed ester in the proportion stated above enhances the dispersability of such esters in lubricant compositions and additive concentrates for lubricant compositions.

Still another essential element of the mixed ester is the extent of esterification in relation to the extent of neutralization of the unesterified carboxy groups of the carboxy-containing interpolymer through the conversion thereof to the optional polyamino-containing groups. For convenience, the relative proportions of the high molecular weight ester group to the low molecular weight ester group and to the polyamino group are expressed in terms of molar ratios of

(50-100);(5-50);(0.1-15), respectively. The preferred ratio is (70-85);(15-30);(3-4). It should be noted that the linkage described as the carbonyl-polyamino group may be imide, amide, or amidine and inasmuch as any such linkage is contemplated within the present invention, the term "carbonyl polyamino" is thought to be a convenient, generic expression useful for the purpose of defining the inventive concept. In a particularly advantageous embodiment of the invention such linkage is imide or predominantly imide.

Still another important element of the mixed ester is the molecular weight of the carboxy-containing interpolymer. For convenience, the molecular weight is expressed in terms of the "reduced specific viscosity" of the interpolymer which is a widely recognized means of expressing the molecular size of a polymeric substance. As used herein, the reduced specific viscosity (abbreviated as RSV) is the value obtained in accordance with the formula

$$\text{RSV} = \frac{\text{Relative Viscosity} - 1}{\text{Concentration}}$$

wherein the relative viscosity is determined by measuring, by means of a dilution viscometer, the viscosity of a solution of one gram of the interpolymer in 10 ml. of acetone and the viscosity of acetone at  $30 \pm 0.02^\circ\text{C}$ . For purpose of computation by the above formula, the concentration is adjusted to 0.4 gram of the interpolymer per 100 ml. of acetone. A more detailed discussion of the reduced specific viscosity, also known as the specific viscosity, as well as its relationship to the average molecular weight of an interpolymer, appears in Paul J. Flory, Principles of Polymer Chemistry, (1953 Edition) pages 308 et seq.

While interpolymers having reduced specific viscosity of from about 0.05 to about 2 are contemplated in the mixed ester, the preferred interpolymers are those having a reduced specific viscosity of from about 0.1 to about 1. In most instances, interpolymers having a reduced specific viscosity of from about 0.1 to about 0.8 are particularly preferred.

From the standpoint of utility, as well as for commercial and economical reasons, esters in which the high molecular weight ester group has from 8 to 24 aliphatic carbon atoms, the low molecular weight ester group has from 3 to 5 carbon atoms, and the carbonyl amino group is derived from a primary-aminoalkyl-substituted tertiary amine, particularly heterocyclic amines, are preferred. Specific examples of the high molecular weight carboxylic ester group, i.e., the (OR) group of the ester radical (i.e., -(O) (OR)) include heptyloxy, isooctyloxy, decyoxy, dodecyloxy, tridecyloxy, tetradecyoxy, pentadecyoxy, octadecyoxy, eicosyloxy, tricosyloxy, tetracosyloxy, etc. Specific examples of low molecular weight groups include methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, sec-butoxy, iso-butoxy, n-pentyloxy, neo-pentyloxy, n-hexyloxy, cyclohexyloxy, xy-

lopentoxy, 2-methyl-butyl-1-oxy, 2,3-dimethyl-butyl-1-oxy, etc. In most instances, alkoxy groups of suitable size comprise the preferred high and low molecular weight ester groups. Polar substituents may be present in such ester groups. Examples of polar substituents are chloro, bromo, ether, nitro, etc.

Examples of the carbonyl polyamine group include those derived from polyamino compounds having one primary or secondary amino group and at least one mono-functional amino group such as tertiary-amino or heterocyclic amino group. Such compounds may thus be tertiary-amino substituted primary or secondary amines or other substituted primary or secondary amines in which the substituent is derived from pyrroles, pyrrolidones, caprolactams, oxazolidones, oxazoles, thiazoles, pyrazoles, pyrazolines, imidazoles, imidazolines, thiazines, oxazines, diazines, oxy carbamyl, thiocarbamyl, uracils, hydantoin, thiohydantoin, guanidines, ureas, sulfonamides, phosphoramides, phenothiazines, amidines, etc. Examples of such polyamino compounds include dimethylamino-ethylamine, dibutylamino-ethylamine, 3-dimethylamino-1-propylamine, 4-methylethylamino-1-butylamine, pyridyl-ethylamine, N-morpholin-6-ethylamine, tetrahydropyridyl-ethylamine, bis(dimethylamino)propyl-amine, bis(diethylamino)ethylamine, N,N-dimethyl-p-phenylene diamine, piperidyl-ethylamine, 1-aminoethyl pyrazole, 1-(methyleno)pyrazoline, 1-methyl-4-amino-octyl pyrazole, 1-aminobutyl imidazole, 4-aminoethyl thiazole, 2-aminoethyl pyridine, ortho-aminoethyl-N,N-dimethylbenzenesulfamide, N-aminoethyl phenothiazine, N-aminoethylacetamide, 1-aminophenyl-2-aminoethyl pyridine, N-methyl-N-aminoethyl-S-ethylthiocarbonate, etc. Preferred polyamino compounds include the N-aminoalkyl-substituted morpholines such as aminopropyl morpholine. For the most part, the polyamino compounds are those which contain only one primary-amino or secondary-amino group and, preferably at least one tertiary-amino group. The tertiary amino group is preferably a heterocyclic amino group. In some instances polyamino compounds may contain up to about 6 amino groups although, in most instances, they contain one primary amino group and either one or two tertiary amino groups. The polyamino compounds may be aromatic or aliphatic amines and are preferably heterocyclic amines such as amino-alkyl-substituted morpholines, pipерazines, pyridines, benzopyrroles, quinolines, pyrroles, etc. They are usually amines having from 4 to about 30 carbon atoms, preferably from 4 to about 12 carbon atoms. Polar substituents may likewise be present in the polyamines.

The carboxy-containing interpolymers include principally interpolymers of alpha, beta-unsaturated acids or anhydrides such as maleic anhydride or itaconic anhydride with olefins (aromatic or aliphatic) such as ethylene, propylene, isobutene or styrene, or substituted styrene wherein the substituent is a hydrocarbyl group containing from 1 up to about 18 carbon atoms. The styrene-maleic anhydride interpolymers are especially useful. They are obtained by polymerizing equal molar amounts of styrene and maleic anhydride, with or without one or more additional interpolymerizable comonomers. In lieu of styrene, an aliphatic olefin may be used, such as ethylene, propylene or isobutene. In lieu of maleic anhydride, acrylic acid or methacrylic acid or ester thereof may be used. Such interpolymers are known in the art and need not be described in detail here. Where an interpolymerizable comonomer is contemplated, it should be present in a relatively minor proportion, i.e., less than about 0.3 mole, usually less than about 0.15 mole, per mole of either the olefin (e.g. styrene) or the alpha, beta-unsaturated acid or anhydride (e.g. maleic anhydride). Various methods of interpolymerizing styrene and maleic anhydride are known in the art and need not be discussed in detail here. For purpose of illustration, the interpolymerizable comonomers include the vinyl monomers such as vinyl acetate, acrylonitrile, methylacrylate, methylmethacrylate, acrylic acid, vinyl methyl ether, vinyl chloride, isobutene or the like.

The nitrogen-containing esters of the mixed ester are most conveniently prepared by first 100 percent esterifying the carboxy-containing interpolymer with a relatively high molecular weight alcohol and a relatively low molecular weight alcohol. When the optional (C) is employed, the high molecular weight alcohol and low molecular weight alcohol are utilized to convert at least about 50% and no more than about 98% of the carboxy radicals of the interpolymer to ester radicals and then neutralizing the remaining carboxy radicals with a polyamino compound such as described above. To incorporate the appropriate amounts of the two alcohol groups into the interpolymer, the ratio of the high molecular weight alcohol to the low molecular weight alcohol used in the process should be within the range of from about 2.1 to about 9.1 on a molar basis. In most instances the ratio is from about 2.5:1 to about 5:1. More than one high molecular weight alcohol or low molecular weight alcohol may be used in the process; so also may be used commercial alcohol mixtures such as the so-called Oxoalcohols which comprise, for example mixtures of alcohols having from 8 to about 24 carbon atoms. A particularly useful class of alcohols are the commercial alcohols or alcohol mixtures comprising decylalcohol, dodecyl alcohol, tridecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, hexadecyl alcohol, heptadecyl alcohol and octadecyl alcohol. Other alcohols useful in the process are illustrated by those which, upon esterification, yield the ester groups exemplified above.

The extent of esterification, as indicated previously, may range from about 50% to about 98% conversion of the carboxy radicals of the interpolymer to ester radicals. In a preferred embodiment, the degree of esterification ranges from about 75% to about 95%.

The esterification can be accomplished simply by heating the carboxy-containing interpolymer and the al-

cohol or alcohols under conditions typical for effecting esterification. Such conditions usually include, for example, a temperature of at least about 80°C, preferably from about 150°C to about 350°C, provided that the temperature be below the decomposition point of the reaction mixture, and the removal of water of esterification as the reaction proceeds. Such conditions may optionally include the use of an excess of the alcohol reactant so as to facilitate esterification, the use of a solvent or diluent such as mineral oil, toluene, benzene, xylene or the like and a esterification catalyst such as toluene sulfonic acid, sulfuric acid, aluminum chloride, boron trifluoride-triethylamine, hydrochloric acid, ammonium sulfate, phosphoric acid, sodium methoxide or the like. These conditions and variations thereof are well known in the art.

A particularly desirable method of effecting esterification involves first reacting the carboxy-containing interpolymers with the relatively high molecular weight alcohol and then reacting the partially esterified interpolymers with the relatively low molecular weight alcohol. A variation of this technique involves initiating the esterification with the relatively high molecular weight alcohol and before such esterification is complete, the relatively low molecular weight alcohol is introduced into the reaction mass so as to achieve a mixed esterification. In either event it has been discovered that a two-step esterification process whereby the carboxy-containing interpolymers is first esterified with the relatively high molecular weight alcohol so as to convert from about 50% to about 75% of the carboxy radicals to ester radicals and then with the relatively low molecular weight alcohol to achieve the finally desired degree of esterification results in products which have unusually beneficial viscosity properties.

The esterified interpolymers may optionally be treated with a polyamino compound in an amount so as to neutralize substantially all of the unesterified carboxy radicals of the interpolymers. The neutralization is preferably carried out at a temperature of at least about 80°C, often from about 120°C to about 300°C, provided that the temperature does not exceed the decomposition point of the reaction mass. In most instances the neutralization temperature is between about 150°C and 250°C. A slight excess of the stoichiometric amount of the amino compound is often desirable, so as to insure substantial completion of neutralization, i.e., no more than about 2% of the carboxy radicals initially present in the interpolymers remained unneutralized.

The following non-limiting examples are illustrative of the preparation of the mixed ester of the present invention. Unless otherwise indicated all parts and percentages are by weight.

#### EXAMPLE (B-1)

A styrene-maleic interpolymers is obtained by preparing a solution of styrene (16.3 parts by weight) and maleic anhydride (12.9 parts) in a benzene-toluene solution (270 parts; weight ratio of benzene:toluene being 66.5:33.5) and contacting the solution at 86°C. in nitrogen atmosphere for 8 hours with a catalyst solution prepared by dissolving 70% benzoyl peroxide (0.42 part) in a similar benzene-toluene mixture (2.7 parts). The resulting product is a thick slurry of the interpolymers in the solvent mixture. To the slurry there is added mineral oil (141 parts) while the solvent mixture is being distilled off at 150°C. and then at 150°C./200 mm. Hg. To 209 parts of the stripped mineral oil-interpolymer slurry (the interpolymers having a reduced specific viscosity of 0.72) there are added toluene (25.2 parts), n-butyl alcohol (4.8 parts), a commercial alcohol consisting essentially of primary alcohols having from 8 to 18 carbon atoms (56.6 parts) and a commercial alcohol consisting of primary alcohols having from 8 to 10 carbon atoms (10 parts) and to the resulting mixture there is added 96% sulfuric acid (2.3 parts). The mixture is then heated at 150°-160°C. for 20 hours whereupon water is distilled off. An additional amount of sulfuric acid (0.18 part) together with an additional amount of n-butyl alcohol (3 parts) is added and the esterification is continued until 95% of the carboxy radicals of the polymer has been esterified. To the esterified interpolymers, there is then added aminopropyl morpholine (3.71 parts; 10% in excess of the stoichiometric amount required to neutralize the remaining free carboxy radicals) and the resulting mixture is heated to 150°-160°C./10 mm. Hg to distill off toluene and any other volatile components. The stripped product is mixed with an additional amount of mineral oil (12 parts) filtered. The filtrate is a mineral oil solution of the nitrogen-containing mixed ester having a nitrogen content of 0.16-0.17%.

#### EXAMPLE (B-2)

The procedure of Example (B-1) is followed except that the esterification is carried out in two steps, the first step being the esterification of the styrene-maleic interpolymers with the commercial alcohols having from 8 to 18 carbon atoms and the second step being the further esterification of the interpolymers with n-butyl alcohol.

#### EXAMPLE (B-3)

The procedure of Example (B-1) is followed except that the esterification is carried out by first esterifying the styrene-maleic interpolymers with the commercial alcohol having from 8 to 18 carbon atoms until 70% of

the carboxyl radicals of the interpolymer have been converted to ester radicals and thereupon continuing the esterification with any yet-unreacted commercial alcohols and n-butyl alcohol until 95% of the carbonyl radicals of the interpolymer have been converted to ester radicals.

5      EXAMPLE (B-4)

The procedure of Example (B-1) is followed except that the interpolymer is prepared by polymerizing a solution consisting of styrene (416 parts), maleic anhydride (392 parts), benzene (2153 parts) and toluene (5025 parts) in the presence of benzoyl peroxide (1.2 parts) at 65°-106°C. (The resulting interpolymer has a reduced specific viscosity of 0.45).

10     EXAMPLE (B-5)

The procedure of Example (B-1) is followed except that the styrene-maleic anhydride is obtained by polymerizing a mixture of styrene (416 parts), maleic anhydride (392 parts), benzene (6101 parts) and toluene (2310 parts) in the presence of benzoyl peroxide (1.2 parts) at 78°-92°C. (The resulting interpolymer has a reduced specific viscosity of 0.91).

15     EXAMPLE (B-6)

The procedure of Example (B-1) is followed except that the styrene-maleic anhydride is prepared by the following procedure: Maleic anhydride (392 parts) is dissolved in benzene (6870 parts). To this mixture there is added styrene (416 parts) at 76°C. whereupon benzoyl peroxide (1.2 parts) is added. The polymerization mixture is maintained at 80-82°C. for about 5 hours. (The resulting interpolymer has a reduced specific viscosity of 1.24.)

20     EXAMPLE (B-7)

The procedure of Example (B-1) is followed except that acetone (1340 parts) is used in place of benzene as the polymerization solvent and that azobisisobutyronitrile (0.3 part) is used in place of benzoyl peroxide as a polymerization catalyst.

25     EXAMPLE (B-8)

An interpolymer (0.86 carboxyl equivalent) of styrene and maleic anhydride (prepared from an equal molar mixture of styrene and maleic anhydride and having a reduced specific viscosity of 0.69) is mixed with mineral oil to form a slurry, and then esterified with a commercial alcohol mixture (0.77 mole; comprising primary alcohols having from 8 to 18 carbon atoms) at 150-160°C. In the presence of a catalytic amount of sulfuric acid until about 70% of the carboxyl radicals are converted to ester radicals. The partially esterified interpolymer is then further esterified with a n-butyl alcohol (0.31 mole) until 95% of the carboxyl radicals of the interpolymer are converted to the mixed ester radicals. The esterified interpolymer is then treated with aminopropyl morpholine (slight excess of the stoichiometric amount to neutralize the free carboxyl radicals of the interpolymer) at 150-160°C. until the resulting product is substantially neutral (acid number of 1 to phenolphthalein indicator). The resulting product is mixed with mineral oil so as to form an oil solution containing 34% of the polymeric product.

30     Examples (B-1) through (B-8) are prepared using mineral oil as the diluent. All of the mineral oil or a portion thereof may be replaced with the triglyceride oil (A). The preferred triglyceride oil is the high oleic sunflower oil.

35     EXAMPLE (B-9)

40     Charged to a 12 liter 4 neck flask is 3621 parts of the interpolymer of Example (B-8) as a toluene slurry. The percent toluene is about 76 percent. Stirring is begun and 933 parts (4.3 equivalents) Alfol 1218 alcohol and 1370 parts xylene are added. The contents are heated and toluene is removed by distillation. Additional xylene is added in increments of 500, 500, 300 and 300 parts while continuing to remove toluene, the object being to replace the lower boiling toluene with the higher boiling xylene. The removal of solvent is stopped when the temperature of 140°C. is reached. The flask is then fitted with an addition funnel and the condenser is set to reflux. At 140°C., 23.6 parts (0.17 equivalents) methanesulfonic acid in 432 parts (3 equivalents) Alfol 810 alcohol is added in about 20 minutes. The contents are stirred overnight at reflux while collecting water in a Dean Stark trap. Then added is 185 parts (2.5 equivalents) of n-butanol containing therein 3.0 parts (0.02

equivalents) of methanesulfonic acid. This addition occurs over a 60 minute time period. The contents are maintained at reflux for 8 hours and then an additional 60 parts (0.8 equivalents) n-butanol is added and the contents are permitted to reflux overnight. At 142°C, is added 49.5 parts (0.34 equivalents) aminopropylmorpholine in 60 minutes. After a 2 hour reflux 13.6 parts (equivalents) 50% aqueous sodium hydroxide is added over 60 minutes and after an additional 60 minutes of stirring there is added 17 parts of an alkylated phenol.

To a 1 liter flask is added 495 parts of the above esterified product. The contents are heated to 140°C, and 337 parts Sunyl® 80 is added. Solvent is removed at 155°C, with nitrogen blowing at 1 cubic foot per hour. The final stripping conditions are 155°C, and 20 mm Hg. At 100°C, the contents are filtered using diatomaceous earth. The filtrate is a vegetable oil solution of the nitrogen-containing mixed ester having a nitrogen content of 0.14%.

Examples (B-10) and (B-11) employ an interpolymerizable monomer as part of the carboxy-containing interpolymer.

#### Example (B-10)

One mole each of maleic anhydride and styrene and 0.05 moles methyl methacrylate are polymerized in toluene in the presence of benzoyl peroxide (1.5 parts) at 75-95°C. The resulting interpolymer has a reduced specific viscosity of 0.13 and is a 12% slurry in toluene. Added to a 2 liter 4 neck flask is 868 parts (1 equivalent) of the polymer along with 68 parts (0.25 equivalents) oleyl alcohol, 55 parts (0.25 equivalents) Neodol 45, 55 parts (0.25 equivalents) Alfol 1218 and 36 parts (0.25 equivalents) Alfol 8-10. The contents are heated to 115°C and added in 2 parts (0.02 moles) methanesulfonic acid. After a 2 hour reaction period, toluene is distilled off. With a neutralization number of 18.7 to phenolphthalein (indicating an 89% esterification), 15 parts (0.20 equivalents) n-butanol is added dropwise over 5 hours. The neutralization number/esterification level is 14.0/92.5%. Then added is 1.6 parts (0.02 moles) 50% aqueous sodium hydroxide to neutralize the catalyst. This is followed by the addition of 5.5 parts (0.038 equivalents) of aminopropylmorpholine and 400 parts Sunyl® 80. The contents are vacuum stripped to 15 millimeters mercury at 100°C and filtered using a diatomaceous earth filter aid. The filtrate is the product containing 0.18 percent nitrogen and 54.9 percent Sunyl® 80.

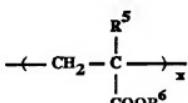
The following example is similar to Example (B-10) but employs different alcohols and different levels in a different order of addition.

#### Example (B-11)

Added to a 2 liter 4 neck flask is 868 parts (1 equivalent) of the polymer of Example (B-10), 9.25 parts (0.125 equivalents) isobutyl alcohol, 33.8 parts (0.125 equivalents) oleyl alcohol, 11 parts each (0.125 equivalents) of 2-methyl-1-butanol, 3-methyl-1-butanol and 1-pentanol, 23.4 parts (0.125 equivalents) hexyl alcohol, and 16.25 parts each (0.125 equivalents) 1-octanol and 2-octanol. At 110°C 2 parts (0.02 moles) methanesulfonic acid is added. One hour later toluene is distilled off and when the distillation is complete, the neutralization number/esterification level is 62.5/70 percent. At 140°C 31.2 parts (0.43 equivalents) n-butanol is added dropwise over 28 hours and the neutralization number/esterification level is 36.0/79.3 percent. At 120°C 0.3 parts (0.03 moles) methanesulfonic acid is added followed by 20.4 parts (0.20 equivalents) hexyl alcohol. After esterification the neutralization number/esterification level is 10.5/95 percent. Then added is 1.9 parts (0.023 moles) of 50% sodium hydroxide followed by 5.9 parts (0.04 equivalents) aminopropylmorpholine and 400 parts Sunyl® 80. The contents are filtered and the product has a nitrogen analysis of 0.18 percent.

#### Acrylate Polymers

In another aspect Component (B) may be at least one hydrocarbon-soluble acrylate polymer of the formula



wherein R<sup>5</sup> is hydrogen or a lower alkyl group containing from 1 to about 4 carbon atoms, R<sup>6</sup> is a mixture of alkyl, cycloalkyl or aromatic groups containing from about 4 to about 24 carbon atoms, and x is an integer providing a weight average molecular weight (Mw) to the acrylate polymer of about 5000 to about 1,000,000.

Preferably R<sup>5</sup> is a methyl or ethyl group and more preferably, a methyl group. R<sup>6</sup> is primarily a mixture of

alkyl groups containing from 4 to about 18 carbon atoms. In one embodiment, the weight average molecular weight of the acrylate polymer is from about 100,000 to about 1,000,000 and in other embodiments, the molecular weight of the polymer may be from 100,000 to about 700,000 and 300,000 to about 700,000.

Specific examples of the alkyl groups R<sup>6</sup> which may be included in the polymers of the present invention include, for example, n-butyl, octyl, decyl, dodecyl, tridecyl, octadecyl, hexadecyl, octadecyl. The mixture of alkyl groups can be varied so long as the resulting polymer is hydrocarbon-soluble.

The following non-limiting examples are illustrative of the preparations of the acrylate polymers of the present invention. All parts and percentages are by weight unless indicated to the contrary.

10 Example (B-12)

Added to a 2 liter 4 neck flask is 50.8 parts (0.20 moles) lauryl methacrylate, 44.4 parts (0.20) isobornyl methacrylate, 38.4 parts (0.20 moles) 2-phenoxy ethyl acrylate, 37.6 parts (0.20 moles) 2-ethylhexyl acrylate, 45.2 parts (0.20 moles) isodecyl methacrylate and 500 parts toluene. At 100°C 1 parts Vazo® 67 (2,2' azois(2-methylbutyronitrile)) in 20 parts toluene is added over 7 hours. The reaction is held at 100°C for 16 hours after which the temperature is increased to 120°C to remove toluene and added is 216 parts of Sunyl® 80. Volatiles are removed by vacuum distillation at 20 millimeters mercury at 140°C. The contents are filtered to give the desired product.

20 Example (B-13)

Added to a 2 liter 4 neck flask is 38.1 parts (0.15 moles) lauryl methacrylate, 48.6 parts (0.15 moles) stearyl acrylate, 28.2 parts (0.15 moles) 2-ethylhexyl methacrylate, 25.5 parts (0.15 moles) tetrahydrofurfuryl methacrylate, 33.9 parts (0.15 moles) isodecyl methacrylate and 500 parts toluene. At 100°C 1 part Vazo® 67 in 20 parts toluene is added dropwise in 6 hours. After the addition is complete, the reaction mixture is held at 100°C for 15.5 hours, toluene is distilled out and 174 parts Sunyl® 80 is added. The contents are vacuum stripped at 140°C at 20 millimeters of mercury and filtered to give the desired product.

An example of a commercially available methacrylate ester polymer which has been found to be useful in the present invention is sold under the tradename of "Acryloid 702" by Rohm and Haas, wherein R<sup>6</sup> is predominantly a mixture of n-butyl, tridecyl, and octadecyl groups. The weight average molecular weight (Mw) of the polymer is about 404,000 and the number average molecular weight (Mn) is about 118,000. Another commercially available methacrylate polymer useful in the present invention is available under the tradename of "Acryloid 954" by Rohm and Haas, wherein R<sup>6</sup> is predominantly a mixture of n-butyl, decyl, tridecyl, octadecyl, and tetradecyl groups. The weight average molecular weight of Acryloid 954 is found to be about 440,000 and the number average molecular weight is about 111,000. Each of these commercially available methacrylate polymers is sold in the form of a concentrate of about 40% by weight of the polymer in a light-colored mineral lubricating oil base. When the polymer is identified by the tradename, the amount of material added is intended to represent an amount of the commercially available Acryloid material including the oil.

Other commercially available polymethacrylates are available from Rohm and Haas Company as Acryloid 1253, Acryloid 1265, Acryloid 1263, Acryloid 1267, from Rohm GmbH as Viscoplex 0-410, Viscoplex 10-930, Viscoplex 5029, from Societe Francaise D'Organo-Synthese as Garbacryl T-84, Garbacryl T-789, from Texaco as TLA 233, TLA 5010 and TC 10124. Some of these polymethacrylates may be PMA/OCP (olefin copolymer) type polymers.

45 Nitrogen-Containing Polyacrylate

Component (B) may also be a nitrogen-containing polyacrylate prepared by reacting an acrylate ester of the formula



55 wherein R<sup>9</sup> is hydrogen or an alkyl group containing from 1 to about 4 carbon atoms and R<sup>10</sup> is an alkyl, cycloalkyl or aromatic group containing from 4 to about 24 carbon atoms with a nitrogen containing compound. For each mole of the acrylate ester from 0.001 - 1.0 moles of the nitrogen containing compound is employed.

The reaction is carried out at a temperature of from 50°C up to about 250°C. Non-limiting examples of nitrogen containing compounds are 4-vinylpyridine, 2-vinylpyridine, 2-n-morpholinioethyl acrylate, N,N-dimethylaminoethyl acrylate, and N,N-dimethylaminopropyl methacrylate.

The following non-limiting example is illustrative of the preparation of the nitrogen-containing polymethacrylate. All parts and percentages are by weight unless indicated otherwise.

Example (B-14)

Added to a 2 liter 4 neck flask is 50.8 parts (0.2 moles) lauryl methacrylate, 44.4 parts (0.20 moles) isobornyl methacrylate, 38.4 parts (0.20 moles) 2-phenoxyethyl acrylate, 37.6 parts (0.20 moles) 2-ethylhexyl acrylate, 45.2 parts (0.20 moles) isodecyl methacrylate, 21 parts (0.20 moles) 4-vinylpyridine and 500 parts toluene. At 100°C 1 part Vazo 67 in 20 parts toluene is added dropwise in 8 hours. After maintaining the temperature at 100°C for an additional 20 hours, an additional 0.5 parts Vazo 67 in 10 parts toluene is added in 3 hours. Toluene is then removed by distillation, 235 parts Sunyl® 80 is added and the contents are vacuum stripped to 25 millimeters mercury at 140°C. The contents are filtered to give a product with 0.71 percent nitrogen.

A few companies that make nitrogen-containing polyacrylates are Rohm and Haas, Rohm GmbH, Texaco, Albright & Wilson, Societe Francaise and D'Organo-Synthese (SFOS).

20 Methylen Linked Aromatic Compounds

Another PPD having utility in this invention is a mixture of compounds having the general structural formula:



25 wherein the Ar, Ar' and Ar'' are independently an aromatic moiety and each aromatic moiety is substituted with 0 to 3 substituents (the preferred aromatic precursor being naphthalene), R<sup>7</sup> and R<sup>8</sup> are independently straight or branch chain alkynes containing 1 to 100 carbon atoms and n is 0 to 1000.

This PPD is characterized by the presence of compounds over a wide molecular weight range. The molecular weight of compounds in the composition of the invention could vary from that of a simple unsubstituted benzene to a polymer of 1000 monomers of trisubstituted naphthalenes linked by alkynes containing as many as 100 carbon atoms with the substituents of the naphthalene containing 1 to 50 carbon atoms.

The substituents for the aromatic moieties are obtained from olefins and/or chlorinated hydrocarbons.

The useful olefins include 1-octene, 1-decene, and alpha-olefins of chain lengths C<sub>12</sub>, C<sub>14</sub>, C<sub>15-18</sub>, C<sub>16-20</sub>, C<sub>20-24</sub>, C<sub>24-28</sub>. More preferably the invention process is carried out with olefins which are mixtures of the above.

35 A good example would be the C<sub>16-20</sub> cracked wax olefins, or a mixture of 1-octene and C<sub>16-18</sub> alpha olefin.

The chlorinated hydrocarbons might contain from 1-50 carbon atoms and from about 2 to about 84% chlorine by weight. Preferred chlorinated hydrocarbons are obtained by chlorinating slack waxes or paraffinic waxes of C<sub>18-30</sub> chain length so that they contain from 5-50% chlorine by weight. A particularly preferred chlorinated hydrocarbon, being one of about 24 carbons containing about 2.5 chlorines per 24 carbon atoms.

40 Although Ar, Ar' and Ar'' may be any aromatic containing 1 to 3 aromatic rings, it is preferable if Ar, Ar' and Ar'' are all the same. Further, it is preferable if Ar, Ar' and Ar'' are fused benzene rings, i.e., when two or three benzene rings are present, the adjoining rings share two carbon atoms. Most preferably, Ar, Ar' and Ar'' are all derived from naphthalene.

45 Aromatics which might be precursors of Ar, Ar' and Ar'' include benzene, biphenyl, diphenylmethane, triphenylmethane, aniline, diphenylamine, diphenylether, phenol, naphthalene, anthracene and phenanthrene. Naphthalene is particularly preferred.

Although the aromatic groups of the general formula above can contain 0 to 3 substituents, the composition will desirably contain compounds with one or two substituents and will preferably include compounds with two substituents. The substituents may be derived from any olefin (preferably an alpha olefin containing 8 to 30 carbon atoms) or derived from a chlorinated hydrocarbon containing 8 to 50 carbon atoms (preferably a chlorinated hydrocarbon derived from a hydrocarbon wax containing 22-26 carbon atoms). In addition to or in place of forming the substituents, the olefin and/or chlorinated hydrocarbon may form the alkyne linking group (R<sup>7</sup> and R<sup>8</sup> group) of the general structural formula. Compositions of the invention might include compounds where in each of the naphthalene groups is substituted with one alkyl group containing 16 to 18 carbon atoms and one derived from a chlorinated hydrocarbon containing about 24 carbon atoms with about 2.5 chlorine atoms present for each 24 carbon atoms.

The desired material is a mixture of products which include alkylated naphthalenes, coupled and bridged

naphthalenes, oligomers and dehydrohalogenated waxes. The mw distribution of the final product is a more useful characterization of the final product. A useful mw range is from 300-2000. A more useful mw range is from 500 to 10,000. A preferred distribution is from 400 to 112,000. The most useful distribution is from about 271 to about 300,000.

- 5      A methylene linked aromatic compound PPD may be produced according to the following general process:  
       (a) providing aromatic compounds containing 1 to 3 aromatic rings which compounds are substituted with  
          0 to 3 substituents, the compounds being precursors for aromatic moieties Ar, Ar' and Ar" in a reactor;  
       (b) adding a FRIEDEL-CRAFTS or Lewis Acid catalyst to the reactor;  
       (c) adding a chlorinated hydrocarbon to the reactor;  
 10     (d) adding an olefin to the reactor and  
       (e) adding  $\text{CH}_2\text{Cl}_2$  to the reactor wherein step (e) is carried out prior to or concurrently with at least one  
          step of (a)-(d).

As indicated above, the aromatic compounds forming Ar, Ar' and Ar" groups in the compound of the general formula are preferably naphthalene. If the aromatic compound is substituted, it is substituted with an alkyl or alkenyl, either of which may be chlorine substituted, branched or straight chain. Accordingly, in accordance with one embodiment of the process of the present invention, naphthalene is mixed with methylene chloride in a reaction flask. At this point, the methylene chloride acts as a solvent. A FRIEDEL-CRAFTS or Lewis Acid catalyst is then added to the mixture. The catalyst is preferably in the form of  $\text{AlC}_1_3$ . After adding the catalyst, a chlorinated hydrocarbon (most preferably one containing 22-26 carbons) is added to the reaction flask and a reaction occurs between the naphthalene and the chlorinated hydrocarbon wax such that the naphthalene is substituted with an alkyl group derived from the chlorinated hydrocarbon wax. Furthermore, linking will occur between naphthalene compounds via methylene group as shown within the general structural formula ( $R^7$ ) or ( $R^8$ ) is  $\text{CH}_2$ .

The mixture is then preferably cooled to a temperature in the range of 0° to 5°C. While continuing to cool 25 the vessel, an olefin (preferably an alpha-olefin containing 8 to 30 carbon atoms) is added slowly so that the temperature is continually maintained in the range of 0°C to 5°C. Alkylation of the naphthalene compounds occurs so that the naphthalenes are substituted with an alkyl group derived from said olefin. The catalyst is decomposed and is neutralized with a base such as lime after which stirring is continued while the temperature is raised first to 60°C and then to 120°C to remove the volatile components of the reaction mixture. The mixture 30 is filtered and the desired product is isolated.

Chlorinated hydrocarbons which may form a substituent on one or more of the aromatic moieties may contain 1 to about 50 carbon atoms. If a chlorinated hydrocarbon containing 50 carbon atoms forms a substituent and is linked to another 50 carbon atom substituent on another aromatic moiety, the aromatic moieties will be linked by an alkylene containing 100 carbons, i.e., ( $R^7$ ) or ( $R^8$ ) is about 100 carbon atoms. However, the aromatic moieties Ar may be linked by a single  $\text{CH}_2$ , i.e., an alkylene containing a single carbon atom wherein ( $R^7$ ) or ( $R^8$ ) is  $\text{CH}_2$ .

The general process for producing this PPD can be carried out over a wide range of ratios of components. To describe the ratio of the components added in steps (a), (b), (c), (d) and (e) the components will be referred to respectively by the letters (a'), (b'), (c'), (d') and (e'). All that is necessary is that (e') be present in sufficient 40 amount so that at least some methylene linking occurs between components (a') and/or that (b'), (c') and (d') be present in sufficient amounts so that there is at least some substitution of (a') by (c') and (d') as catalyzed by (b'). The components (a'), (b'), (c'), (d') and (e') might be present in weight ratios of (a'): (b'): (c'): (d'): (e') in the ranges of about (1):(0.01-1):(0.5-6):(0.5-22):(1-40) and most preferably (1):(0.2):(3):(11):(20); all ratios are in parts by weight.

45      The process can be carried out over a wide range of temperatures above the freezing point and up to the boiling points of the reaction mixture present at any point in steps (a)-(e). The boiling point of (e'), i.e., methylene chloride is about 40°C, however, the maximum reaction temperature may be higher or lower than 40°C at atmospheric pressure due to the presence of other reactants. The process has been carried out at subatmospheric or superatmospheric pressure.

50      EXAMPLE B-10

Naphthalene is mixed with seven parts of  $\text{CH}_2\text{Cl}_2$  and 0.2 parts of  $\text{AlC}_1_3$ . Chlorinated hydrocarbon (2.7 parts) is added slowly into the reaction mixture at 15°C. The reaction mixture is held for 5 hours at ambient 55 temperature or until the release of  $\text{HCl}$  is complete. The mixture is then cooled to about 5°C and 7.3 parts of an alpha olefin mixture is added over 2 hours while maintaining the temperature of the reaction mixture between 0 and 10°C.

The catalyst is decomposed by the careful addition of 0.8 parts 50% aqueous NaOH. The aqueous layer

is separated and the organic layer is purged with N<sub>2</sub> and heated to 140°C and 3mm Hg to remove the volatiles. The residue is filtered to yield 97% of the theoretical yield weight of the product.

(C) The Additive

5

In addition to components (A) and (B) the compositions of this invention may also include (C) an additive. The performance may be enhanced by these additives in the areas of anti-wear, oxidation inhibition, rust/corrosion inhibition, metal passivation, extreme pressure, friction modification, viscosity modification, foam inhibition, emulsification, demulsification, lubricity, dispersancy and detergency and the like.

10

The additive (C) may be selected from

(1) a compound of the formula R<sup>11</sup>A wherein R<sup>11</sup> is an aliphatic group containing from about 6 to about 24 carbon atoms and A is -COOH and/or -OH or -NO<sub>2</sub>;

(2) a Schiff base;

(3) a carboxylic dispersant composition; or

15

(4) an antioxidant.

(C) (1) The R<sup>11</sup>A Compound

20

The R<sup>11</sup>A compound is either a carboxylic acid or alcohol or a mixture thereof or an organic nitrate. When A is -COOH, R<sup>11</sup> preferably contains from 12 to about 24 carbon atoms and most preferably from about 14 to about 20 carbon atoms. The most preferred carboxylic acid is oleic acid.

When A is -OH, R<sup>11</sup> preferably contains from 6 to about 12 carbon atoms. Preferred alcohols are the isomeric octyl alcohols, especially iso octyl alcohol.

25

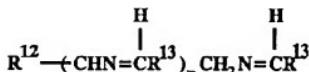
When A is -NO<sub>2</sub>, R<sup>11</sup> preferably contains from 6 to about 12 carbon atoms. Preferred nitrates are the isomeric octyl nitrates, especially 2-ethylhexyl nitrate.

(C) (2) The Schiff Base

30

A Schiff base which may be used in this invention is of the formula

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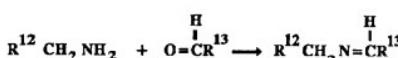


wherein R<sup>12</sup> is an aliphatic group containing from 1 to about 8 carbon atoms and R<sup>13</sup> is an aliphatic group containing from 1 to about 18 carbon atoms or an aromatic or substituted aromatic group containing from 6 to about 18 carbon atoms and n is 0 or 1.

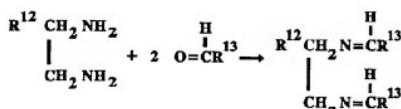
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The Schiff base is formed by the reaction of a primary amine with an aldehyde. The amine may be a mono primary amine such that n is 0 or a vicinal di primary amine such that n is 1.

45



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55

The following Table I is directed to the preparation of Schiff bases. The amine is added dropwise to the aldehyde or vice-versa, and the contents are heated until the desired amount of water is obtained.

TABLE I

| Example No. C-2 | Primary Amine     | Aldehyde            | n |
|-----------------|-------------------|---------------------|---|
| 1               | dodecylamine      | n-butylaldehyde     | 0 |
| 2               | t-butylamine      | benzaldehyde        | 0 |
| 3               | ethylene diamine  | p-tolualdehyde      | 1 |
| 4               | propylenediamine  | salicylaldehyde     | 1 |
| 5               | 2-ethylhexylamine | p-nitrobenzaldehyde | 0 |

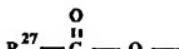
## 15 (C) (3) The Carboxylic Dispersant Composition

The carboxylic dispersant composition is characterized by the presence within its molecular structure of (i) at least one polar group selected from acyl, acyloxy or hydrocarbyl-imidoyl groups, and (ii) at least one group in which a nitrogen or oxygen atom is attached directly to said group (i), and said nitrogen or oxygen atom also is attached to a hydrocarbyl group. The structures of the polar group (i), as defined by the International Union of Pure and Applied Chemistry, are as follows (R<sup>27</sup> representing a hydrocarbon or similar group):

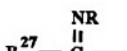
Acyl:



Acyloxy:



Hydrocarbylimidoyl:



40 Group (ii) is preferably at least one group in which a nitrogen or oxygen atom is attached directly to said polar group, said nitrogen or oxygen atom also being attached to a hydrocarbon group or substituted hydrocarbon group, especially an amino, alkylamino-, polyalkyleneamino-, hydroxy- or alkyleneoxy-substituted hydrocarbon group. With respect to group (ii), the dispersants are conveniently classified as "nitrogen-bridged dispersants" and "oxygen-bridged dispersants" wherein the atom attached directly to polar group (i) is nitrogen or oxygen, respectively.

45 Generally, the carboxylic dispersants can be prepared by the reaction of a hydrocarbon-substituted succinic acid-producing compound (herein sometimes referred to as the "succinic acylating agent") with at least about one-half equivalent, per equivalent of acid-producing compound, of an organic hydroxy compound, or an amine containing at least one hydrogen attached to a nitrogen group, or a mixture of said hydroxy compound and amine. The carboxylic dispersants (C-4) obtained in this manner are usually complex mixtures whose precise composition is not readily identifiable. The nitrogen-containing carboxylic dispersants are sometimes referred to herein as "acylated amines". The compositions obtained by reaction of the acylating agent and alcohols are sometimes referred to herein as "carboxylic ester" dispersants. The carboxylic dispersants (C-3) are

either oil-soluble, or they are soluble in the oil-containing lubricating and functional fluids of this invention.

The soluble nitrogen-containing carboxylic dispersants useful as component (C-3) in the compositions of the present invention are known in the art and have been described in many U.S. patents including

|    |           |           |           |
|----|-----------|-----------|-----------|
| 5  | 3,172,892 | 3,341,542 | 3,630,904 |
|    | 3,219,666 | 3,444,170 | 3,787,374 |
|    | 3,272,746 | 3,454,607 | 4,234,435 |
| 10 | 3,316,177 | 3,541,012 |           |

The carboxylic ester dispersants useful as (C-3) also have been described in the prior art. Examples of patents describing such dispersants include U.S. Patents 3,381,022; 3,522,179; 3,542,678; 3,957,855; and 4,034,038. Carboxylic dispersants prepared by reaction of acylating agents with alcohols and amines or amino alcohols are described in, for example, U.S. Patents, 3,576,743 and 3,632,511.

In general, a convenient route for the preparation of the nitrogen-containing carboxylic dispersants (C-3) comprises the reaction of a hydrocarbon-substituted succinic acid-producing compound ("carboxylic acid acylating agent") with an amine containing at least one hydrogen attached to a nitrogen atom (i.e., H-N<). The hydrocarbon-substituted succinic acid-producing compounds include the succinic acids, anhydrides, halides and esters. The number of carbon atoms in the hydrocarbon substituent on the succinic acid-producing compound may vary over a wide range provided that the nitrogen-containing composition (C-3) is soluble in the lubricating compositions of the present invention. Thus, the hydrocarbon substituent generally will contain an average of at least about 12 aliphatic carbon atoms and preferably will contain an average of at least about 50 aliphatic carbon atoms. In addition to the oil-solubility considerations, the lower limit on the average number of carbon atoms in the substituent also is based upon the effectiveness of such compounds in the lubricating oil compositions of the present invention. The hydrocarbyl substituent of the succinic compound may contain polar groups as indicated above, and, providing that the polar groups are not present in proportion sufficiently large to significantly alter the hydrocarbon character of the substituent.

The sources of the substantially hydrocarbon substituent include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-pentene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. They are illustrated by 2-butene, 2-pentene, and 4-octene.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene; isobutene with butadiene; propene with isoprene, ethylene with piperylene; isobutene with chloroprene; isobutene with p-methyl styrene; 1-hexene with 1,3-hexadiene; 1-octene with 1-hexene; 1-heptene with 1-pentene; 3-methyl-1-butene with 1-octene; 3,3-dimethyl-1-pentene with 1-hexene; isobutene with styrene and piperylene; etc.

The relative proportions of the mono-olefins to the other monomers in the interpolymers influence the stability and oil-solubility of the final products derived from such interpolymers. Thus, for reasons of oil-solubility and stability the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, preferably at least about 95%, on a weight basis of units derived from the aliphatic monoolefins and no more than about 5% of olefinic linkages based on the total number of carbon-to-carbon covalent linkages. In most instances, the percentage of olefinic linkages should be less than about 2% of the total number of carbon-to-carbon covalent linkages.

Specific examples of such interpolymers include copolymer of 95% (by weight) of isobutene with 5% of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene, terpolymer of 80% of isobutene with 20% of 1-pentene and 20% of 1-octene; copolymer of 80% of 1-hexene and 20% of 1-heptene; terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and copolymer of 80% of ethylene and 20% of propene.

Another source of the substantially hydrocarbon group comprises saturated aliphatic hydrocarbons such as highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefin polymers illustrated above or high molecular weight olefinic substances.

The use of olefin polymers having molecular weights (Mn) of about 700-10,000 is preferred. Higher molecular weight olefin polymers having molecular weights (Mn) from about 10,000 to about 100,000 or higher

have been found to impart also viscosity index improving properties to the final products of this invention. The use of such higher molecular weight olefin polymers often is desirable. Preferably the substituent is derived from a polyolefin characterized by an Mn value of about 700 to about 10,000, and an Mw/Mn value of 1.0 to about 4.0.

- 5 In preparing the substituted succinic acylating agents of this invention, one or more of the above-described polyalkenes is reacted with one or more acidic reactants selected from the group consisting of maleic or fumaric reactants such as acids or anhydrides. Ordinarily the maleic or fumaric reactants will be maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. The maleic reactants are usually preferred over the fumaric reactants because the former are more readily available and are, in general, more readily reacted with the polyalkenes (or derivatives thereof) to prepare the substituted succinic acid-producing compounds useful in the present invention. The especially preferred reactants are maleic acid, maleic anhydride, and mixtures of these. Due to availability and ease of reaction, maleic anhydride will usually be employed.
- 10 15 For convenience and brevity, the term "maleic reactant" is often used hereinafter. When used, it should be understood that the term is generic to acidic reactants selected from maleic and fumaric reactants including a mixture of such reactants. Also, the term "succinic acylating agents" is used herein to represent the substituted succinic acid-producing compounds.

- 10 One procedure for preparing the substituted succinic acylating agents useful in this invention is illustrated, in part, in U.S. Patent 3,219,666. This procedure is conveniently designated as the "two-step procedure". It involves first chlorinating the polyalkene until there is an average of at least about one chloro group for each molecular weight of polyalkene. (For purposes of this invention, the molecular weight of the polyalkene is the weight corresponding to the Mn value.) Chlorination involves merely contacting the polyalkene with chlorine gas until the desired amount of chlorine is incorporated into the chlorinated polyalkene. Chlorination is generally carried out at a temperature of about 75°C to about 125°C. If a diluent is used in the chlorination procedure, it should be one which is not itself readily subject to further chlorination. Poly- and perchlorinated and/or fluorinated alkanes and benzenes are examples of suitable diluents.

- 25 The second step in the two-step chlorination procedure, for purposes of this invention, is to react the chlorinated polyalkene with the maleic reactant at a temperature usually within the range of about 100°C to about 200°C. The mole ratio of chlorinated polyalkene to maleic reactant is usually about 1:1. (For purposes of this invention, a mole of chlorinated polyalkene is that weight of chlorinated polyalkene corresponding to the Mn value of the unchlorinated polyalkene.) However, a stoichiometric excess of maleic reactant can be used, for example, a mole ratio of 1:2. If an average of more than about one chloro group per molecule of polyalkene is introduced during the chlorination step, then more than one mole of maleic reactant can react per molecule of chlorinated polyalkene. Because of such situations, it is better to describe the ratio of chlorinated polyalkene to maleic reactant in terms of equivalents. (An equivalent weight of chlorinated polyalkene, for purposes of this invention, is the weight corresponding to the Mn value divided by the average number of chloro groups per molecule of chlorinated polyalkene while the equivalent weight of a maleic reactant is its molecular weight.) Thus, the ratio of chlorinated polyalkene to maleic reactant will normally be such as to provide about one equivalent of maleic reactant for each mole of chlorinated polyalkene up to about one equivalent of maleic reactant for each equivalent of chlorinated polyalkene with the understanding that it is normally desirable to provide an excess of maleic reactant; for example, an excess of about 5% to about 25% by weight. Unreacted excess maleic reactant may be stripped from the reaction product, usually under vacuum, or reacted during a further stage of the process as explained below.

- 35 40 The resulting polyalkene-substituted succinic acylating agent is, optionally, again chlorinated if the desired number of succinic groups are not present in the product. If there is present, at the time of this subsequent chlorination, any excess maleic reactant from the second step, the excess will react as additional chlorine is introduced during the subsequent chlorination. Otherwise, additional maleic reactant is introduced during and/or subsequent to the additional chlorination step. This technique can be repeated until the total number of succinic groups per equivalent weight of substituent groups reaches the desired level.

- 45 Another procedure for preparing substituted succinic acid acylating agents useful in this invention utilizes a process described in U.S. Patent 3,912,764 and U.K. Patent 1,440,219.

- 50 According to that process, the polyalkene and the maleic reactant are first reacted by heating them together in a "direct alkylation" procedure. When the direct alkylation step is completed, chlorine is introduced into the reaction mixture to promote reaction of the remaining unreacted maleic reactants. According to the patents, 0.3 to 2 or more moles of maleic anhydride are used in the reaction for each mole of olefin polymer; i.e., polyalkylene. The direct alkylation step is conducted at temperatures of 180-250°C. During the chlorine-introducing stage, a temperature of 160-225°C is employed. In utilizing this process to prepare the substituted succinic acylating agents of this invention, it would be necessary to use sufficient maleic reactant and chlorine to incorporate at least 1.3 succinic groups into the final product for each equivalent weight of polyalkene.

Another process for preparing the substituted succinic acylating agents of this invention is the so-called "one-step" process. This process is described in U.S. Patents 3,215,707 and 3,231,587.

Basically, the one-step process involves preparing a mixture of the polyalkene and the maleic reactant containing the necessary amounts of both to provide the desired substituted succinic acylating agents of this invention. This means that there must be at least one mole of maleic reactant for each mole of polyalkene in order that there can be at least one succinic group for each equivalent weight of substituent groups. Chlorine is then introduced into the mixture, usually by passing chlorine gas through the mixture with agitation, while maintaining a temperature of at least about 140°C.

A variation of this process involves adding additional maleic reactant during or subsequent to the chlorine introduction but, for reasons explained in U.S. Patents 3,215,707 and 3,231,587, this variation is presently not as preferred as the situation where all the polyalkene and all the maleic reactant are first mixed before the introduction of chlorine.

Usually, where the polyalkene is sufficiently fluid at 140° and above, there is no need to utilize an additional substantially inert, normally liquid solvent/diluent in the one-step process. However, as explained hereinbefore, if a solvent/diluent is employed, it is preferably one that resists chlorination. Again, the poly- and perchlorinated and/or -fluorinated alkanes, cycloalkanes, and benzenes can be used for this purpose.

Chlorine may be introduced continuously or intermittently during the one-step process. The rate of introduction of the chlorine is not critical although, for maximum utilization of the chlorine, the rate should be about the same as the rate of consumption of chlorine in the course of the reaction. When the introduction rate of chlorine exceeds the rate of consumption, chlorine is evolved from the reaction mixture. It is often advantageous to use a closed system, including superatmospheric pressure, in order to prevent loss of chlorine so as to maximize chlorine utilization.

The minimum temperature at which the reaction in the one-step process takes place at a reasonable rate is about 140°C. Thus, the minimum temperature at which the process is normally carried out is in the neighborhood of 140°C. The preferred temperature range is usually between about 160-220°C. Higher temperatures such as 250°C or even higher may be used but usually with little advantage. In fact, temperatures in excess of 220°C are often disadvantageous with respect to preparing the particular acylated succinic compositions of this invention because they tend to "crack" the polyalkenes (that is, reduce their molecular weight by thermal degradation) and/or decompose the maleic reactant. For this reason, maximum temperatures of about 200-210°C are normally not exceeded. The upper limit of the useful temperature in the one-step process is determined primarily by the decomposition point of the components in the reaction mixture including the reactants and the desired products. The decomposition point is that temperature at which there is sufficient decomposition of any reactant or product such as to interfere with the production of the desired products.

In the one-step process, the molar ratio of maleic reactant to chlorine is such that there is at least about one mole of chlorine for each mole of maleic reactant to be incorporated into the product. Moreover, for practical reasons, a slight excess, usually in the neighborhood of about 5% to about 30% by weight of chlorine, is utilized in order to offset any loss of chlorine from the reaction mixture. Larger amounts of excess chlorine may be used but do not appear to produce any beneficial results.

The molar ratio of polyalkene to maleic reactant preferably is such that there is at least about one mole of maleic reactant for each mole of polyalkene. This is necessary in order that there can be at least 1.0 succinic group per equivalent weight of substituent group in the product. Preferably, however, an excess of maleic reactant is used. Thus, ordinarily about 5% to about 25% excess of maleic reactant will be used relative to that amount necessary to provide the desired number of succinic groups in the product.

The amines which are reacted with the succinic acid-producing compounds to form the nitrogen-containing compositions (C-3) may be monoamines and polyamines. The monoamines and polyamines must be characterized by the presence within their structure of at least one H-H< group. Therefore, they have at least one primary (i.e., H<sub>2</sub>N-) or secondary amino (i.e., 1 H-N<) group. The amines can be aliphatic, cycloaliphatic, aromatic, or heterocyclic, including aliphatic-substituted cycloaliphatic, aliphatic-substituted aromatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic-substituted alicyclic, and heterocyclic-substituted aromatic amines and may be saturated or unsaturated. The amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction of the amines with the acylating reagents of this invention. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl mercapto, nitro, interrupting groups such as -O- and -S- (e.g., as in such groups as -CH<sub>2</sub>CH<sub>2</sub>-X-CH<sub>2</sub>CH<sub>2</sub>- where X is -O- or -S-). In general, the amine of (C-3) may be characterized by the formula



wherein R<sup>14</sup> and R<sup>15</sup> are each independently hydrogen or hydrocarbon, amino-substituted hydrocarbon, hy-

droxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, amino, carbamyl, thiocarbamyl, guanyl and acylimidoyl groups provided that only one of R<sup>14</sup> and R<sup>15</sup> may be hydrogen.

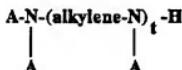
With the exception of the branched polyalkylene polyamine, the polyoxyalkylene polyamines, and the high molecular weight hydrocarbyl-substituted amines described more fully hereafter, the amines ordinarily contain less than about 40 carbon atoms in total and usually not more than about 20 carbon atoms in total.

Aliphatic monoamines include mono-aliphatic and dialiphatic substituted amines wherein the aliphatic groups can be saturated or unsaturated and straight or branched chain. Thus, they are primary or secondary aliphatic amines. Such amines include, for example, mono- and dialkyl-substituted amines, mono- and di-alkenyl-substituted amines, and amines having one N-alkenyl substituent and one N-alkyl substituent and the like. The total number of carbon atoms in these aliphatic monoamines will, as mentioned before, normally not exceed about 40 and usually not exceed about 20 carbon atoms. Specific examples of such monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleyl-amine, N-methyl-octylamine, dodecylamine, octadecylamine, and the like. Examples of cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic amines, and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine, benzylamine, phenethylamine, and 3-(furylpropyl) amine.

Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen through a carbon atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines, N-ethyl-cyclohexylamine, dicyclohexylamines, and the like. Examples of aliphatic-substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic monoamines include propyl-substituted cyclohexylamines, phenyl-substituted cyclopentylamines, and pyranyl-substituted cyclohexylamine.

Aromatic amines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic monoamines include aniline, di-(paramethylphenyl)amine, napthylamine, N,N-dibutyl aniline, and the like. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines are para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted napthylamine, and thienyl-substituted aniline.

The polyamines from which (C-3) is derived include principally alkylene amines conforming for the most part to the formula



wherein t is an integer preferably less than about 10, A is a hydrogen group or a substantially hydrocarbon group preferably having up to about 30 carbon atoms, and the alkylene group is preferably a lower alkylene group having less than about 8 carbon atoms. The alkylene amines include principally methylene amines, ethylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines. They are exemplified specifically by: ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene) triamine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk and Othmer, Vol. 5, pp. 898-905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia. The reaction results in the production of somewhat complex mixtures of alkylene amines, including cyclic condensation products such as piperazines. These mixtures find use in the process of this invention. On the other hand, quite satisfactory products may be obtained also by the use of pure alkylene amines. An especially useful alkylene amine for reasons of economy as well as effectiveness of the products derived therefrom is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia and having a composition which corresponds to that of tetraethylene pentamine.

Hydroxylalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxylalkyl substituents on the nitrogen atoms, likewise are contemplated for use herein. The hydroxylalkyl-substituted alkylene amines are preferably those in which the alkyl group is a lower alkyl group, i.e., having less than about 6 carbon

atoms. Examples of such amines include N-(2-hydroxyethyl)ethylene diamine, N,N'-bis(2-hydroxy-ethyl)-ethylene diamine, 1-(2-hydroxyethyl)piperazine, mono(hydroxymethyl)piperazine, di-hydroxymethyl-substituted tetraethylene pentamine, N-(3-hydroxymethyl)-tetramethylene diamine, and 2-heptadecyl-1-(2-hydroxyethyl)-imidazoline.

5 Higher homologues such as are obtained by condensation of the above illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful. It will be appreciated that condensation through amino radicals results in a high amine accompanied with removal of ammonia and that condensation through the hydroxy radicals results in products containing ether linkages accompanied with removal of water.

10 Heterocyclic mono- and polyamines can also be used in making the nitrogen-containing compositions (C-3). As used herein, the terminology "heterocyclic mono- and polyamine(s)" is intended to describe those heterocyclic amines containing at least one primary secondary amino group and at least one nitrogen as a heteroatom in the heterocyclic ring. However, as long as there is present in the heterocyclic mono- and polyamines at least one primary or secondary amino group, the hetero-N atom in the ring can be a tertiary amino nitrogen; that is, one that does not have hydrogen attached directly to the ring nitrogen. Heterocyclic amines can be saturated or unsaturated and can contain various substituents such as nitro, alkoxy, alkyl mercapto, alkyl, alkenyl, aryl, alkaryl, or aralkyl substituents. Generally, the total number of carbon atoms in the substituents will not exceed about 20. Heterocyclic amines can contain hetero atoms other than nitrogen, especially oxygen and sulfur. Obviously they can contain more than one nitrogen hetero atom. The 5- and 6-membered heterocyclic rings are preferred.

15 Among the suitable heterocyclics are aziridines, azetidines, azolidines, tetra- and di-hydro pyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-di-aminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl-substituted piperidines, piperazine, aminoalkyl-substituted piperazines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminoisopropylmorpholine, N-aminoethylpiperazine, and N,N'-di-aminoethylpiperazine.

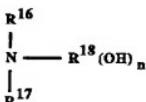
20 The nitrogen-containing composition (C-3) obtained by reaction of the succinic acid-producing compounds and the amines described above may be amine salts, amides, imides, imidazolines as well as mixtures thereof. To prepare the nitrogen-containing composition (C-3), one or more of the succinic acid-producing compounds and one or more of the amines are heated, optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent at an elevated temperature generally in the range of from about 80°C up to the decomposition point of the mixture or the product. Normally, temperatures in the range of about 100°C up to about 300°C are utilized provided that 300°C does not exceed the decomposition point.

25 The succinic acid-producing compound and the amine are reacted in amounts sufficient to provide at least about one-half equivalent, per equivalent of acid-producing compound, of the amine. Generally, the maximum amount of amine present will be about 2 moles of amine per equivalent of succinic acid-producing compound. For the purposes of this invention, an equivalent of the amine is that amount of the amine corresponding to the total weight of amine divided by the total number of nitrogen atoms present. Thus, octyl amine has an equivalent weight equal to its molecular weight; ethylene diamine has an equivalent weight equal to one-half its molecular weight; and aminoethyl piperazine has an equivalent weight equal to one-third its molecular weight. The number of equivalents of succinic acid-producing compound will vary with the number of succinic groups present therein, and generally, there are two equivalents of acylating reagent for each succinic group in the acylating reagents. Conventional techniques may be used to determine the number of carboxyl functions (e.g., acid number, saponification number) and, thus, the number of equivalents of acylating reagent available to react with amine. Additional details and examples of the procedures for preparing the nitrogen-containing compositions of the present invention by reaction of succinic acid-producing compounds and amines are included in, for example, U.S. Patents 3,172,892; 3,219,666; 3,272,746; and 4,234,435.

30 Oxygen-bridged dispersants comprise the esters of the above-described carboxylic acids, as described (for example) in the aforementioned U.S. Patents 3,381,022 and 3,542,678. As such, they contain acyl or occasionally, acylimidoyl groups. (An oxygen-bridged dispersant containing an acyloxy group as the polar group would be a peroxide, which is unlikely to be stable under all conditions of use of the compositions of this invention.) These esters are preferably prepared by conventional methods, usually the reaction (frequently in

the presence of an acidic catalyst) of the carboxylic acid-producing compound with an aromatic compound such as a phenol or naphthol. The preferred hydroxy compounds are alcohols containing up to about 40 aliphatic carbon atoms. These may be monohydric alcohols such as methanol, ethanol, isooctanol, dodecanol, cyclohexanol, neopentyl alcohol, monomethyl ester of ethylene glycol and the like, or polyhydric alcohols including 5 ethylene glycol, diethylene glycol, dipropylene glycol, tetramethylene glycol, pentaerythritol, tris(hydroxymethyl)aminomethane (THAM), glycerol and the like. Carbohydrates (e.g., sugars, starches, cellulose) are also suitable as are partially esterified derivatives of polyhydric alcohols having at least three hydroxy groups.

An especially preferred hydroxy compound reacted with the succinic acid producing compound is an organic hydroxy compound of the formula  
10



20 wherein R<sup>16</sup> and R<sup>17</sup> are aliphatic groups independently containing from 1 up to about 8 carbon atoms, R<sup>18</sup> is an aliphatic group containing from 1 up to about 8 carbon atoms and n is from 1 to about 3. Preferably R<sup>16</sup>, R<sup>17</sup> and R<sup>18</sup> contain up to 3 carbon atoms and n is 1. Most preferably the hydroxy compound is N,N-dimethyl-ethanol amine.

The reaction is usually effected at a temperature above about 100°C and typically at 150-300°C. The esters 25 may be neutral or acidic, or may contain unesterified hydroxy groups, according as the ratio or equivalents of acid-producing compound to hydroxy compound is equal to, greater than or less than 1:1.

As will be apparent, the oxygen-bridged dispersants are normally substantially neutral or acidic. They are among the preferred ester dispersants for the purposes of this invention.

It is possible to prepare mixed oxygen- and nitrogen-bridged dispersants by reacting the acylating agent 30 simultaneously or, preferably, sequentially with nitrogen-containing and hydroxy reagents may be between about 10:1 and 1:10, on an equivalent weight basis. The methods of preparation of the mixed oxygen- and nitrogen-bridged dispersants are generally the same as for the individual dispersants described, except that two sources of group (ii) are used. As previously noted, substantially neutral or acidic dispersants are preferred, and a typical method of producing mixed oxygen- and nitrogen-bridged dispersants of this type (which are especially preferred) is to react the acylating agent with the hydroxy reagent first and subsequently react the intermediate thus obtained with a suitable nitrogen-containing reagent in an amount to afford a substantially neutral or acid product.

The following non-limiting examples are illustrative of the process for preparing the carboxylic dispersant compositions useful in this invention:

40 Example (C-3)-1

A polyisobutylene succinic anhydride is prepared by the reaction of a chlorinated polyisobutylene with maleic anhydride at 200°C. The polyisobutylene group has an average molecular weight of 850 and the resulting alkenyl succinic anhydride is found to have an acid number of 113 (corresponding to an equivalent weight of 500). To a mixture of 500 grams (1 equivalent) of this polyisobutylene succinic anhydride and 160 grams of toluene there is added at room temperature 35 grams (1 equivalent) of diethylene triamine. The addition is made portionwise throughout a period of 15 minutes, and an initial exothermic reaction caused the temperature to rise to 50°C. The mixture then is heated and a water-toluene azeotrope distilled from the mixture. When no more water distills, the mixture is heated to 150°C at reduced pressure to remove the toluene. The residue is diluted with 350 grams of mineral oil and this solution is found to have a nitrogen content of 1.6%.

Example (C-3)-2

55 The procedure of Example (C-3)-1 is repeated using 31 grams (1 equivalent) of ethylene diamine as the amine reactant. The nitrogen content of the resulting product is 1.4%.

Example (C-3)-3

The procedure of Example (C-3)-1 is repeated using 55.5 grams (1.5 equivalents) of an ethylene amine mixture having a composition corresponding to that of triethylene tetramine. The resulting product has a nitrogen content of 1.9%.

Example (C-3)-4

The procedure of Example (C-3)-1 is repeated using 55.0 grams (1.5 equivalents) of triethylene tetramine as the amine reactant. The resulting product has a nitrogen content of 2.9%.

Example (C-3)-5

An acylated nitrogen composition is prepared according to the procedure of Example (C-3)-1 except that the reaction mixture consists of 3800 grams of the polyisobutene succinic anhydride, 376 grams of a mixture of triethylene tetramine and diethylene triamine (75:25 weight ratio), and 2785 grams of mineral oil. The product is found to have a nitrogen content of 2%.

Example (C-3)-6

A mixture of 510 parts (0.28 mole) of polyisobutene ( $M_n=1845$ ;  $M_w=5325$ ) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is the desired polyisobutene-substituted succinic acylating agent having a saponification equivalent number of 87 as determined ASTM procedure D-94.

A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having from about 3 to about 10 nitrogen atoms per molecule to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent at 130°C. The reaction mixture is heated to 150°C in 2 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product.

Example (C-3)-7

A mixture of 100 parts (0.495 mole) of polyisobutene ( $M_n=2020$ ;  $M_w=6049$ ) and 115 parts (1.17 moles) of maleic anhydride is heated to 100°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen blowing for 28 hours. The residue is the desired polyisobutene-substituted succinic acylating agent having a saponification equivalent number of 87 as determined by ASTM procedure D-94.

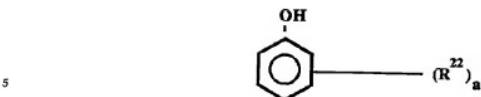
A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamine having from about 3 to 10 nitrogen atoms per molecule to 1067 parts of mineral oil and 893 parts (1.38 equivalents) of the substituted succinic acylating agent at 140-145°C. The reaction mixture is heated to 155°C in 3 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product.

Example (C-3)-8

Added to 1000 parts (3.09 moles) of hexadecyl succinic anhydride is 278 parts (3.12 moles) of N,N-dimethylhexadecylamine. The contents are heated to 93°C and held for 1 hour. The product has a nitrogen content of 3.3%.

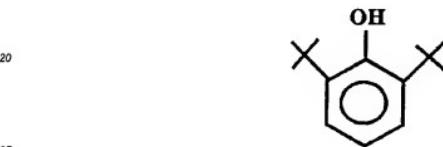
(C) (4) The Antioxidant

Antioxidants which may be used according to the invention include alkyl phenols, benzotriazoles and aromatic amines. The alkyl phenol may have the formula



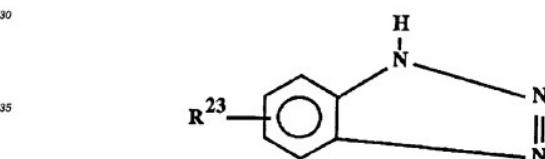
wherein R<sup>22</sup> is an alkyl group containing from 1 up to about 24 carbon atoms and a is an integer of from 1 up to 5. Preferably R<sup>22</sup> contains from 4 to 18 carbon atoms and most preferably from 4 to 12 carbon atoms. R<sup>22</sup> may be either straight chained or branched chained and branched chained is preferred. The preferred value for a is an integer of from 1 to 4 and most preferred is from 1 to 3. An especially preferred value for a is 2. When a is not 5, it is preferred that the position para to the OH group be open.

10 Mixtures of alkyl phenols may be employed. Preferably the phenol is a butyl substituted phenol containing 2 or 3 t-butyl groups. When a is 2, the t-butyl groups occupy the 2,6-position, that is, the phenol is sterically hindered:

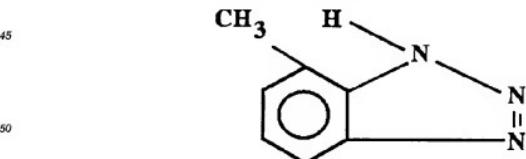


When a is 3, the t-butyl groups occupy the 2,4,6-position.

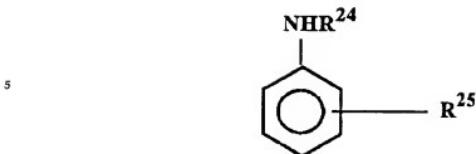
The benzotriazole compound may have the formula



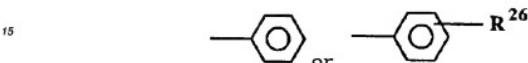
40 wherein R<sup>23</sup> is hydrogen a straight or branched-chain alkyl group containing from 1 up to about 24 carbon atoms, preferably 1 to 12 carbon atoms and most preferably 1 carbon atom. When R<sup>23</sup> is 1 carbon atom the benzotriazole compound is tolyltriazole of the formula



Tolyltriazole is available under the trade name Cobratec TT-100 from Sherwin-Williams Chemical.  
55 The aromatic amine may have the formula



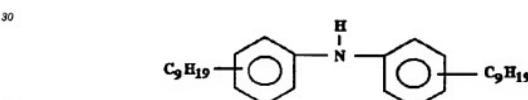
wherein R<sup>24</sup> is



and R<sup>25</sup> and R<sup>26</sup> are independently a hydrogen or an alkyl group containing from 1 up to 24 carbon atoms. Preferably R<sup>24</sup> is



25 and R<sup>25</sup> and R<sup>26</sup> are alkyl groups containing from 4 up to about 20 carbon atoms. In a particularly advantageous embodiment, component (C) comprises an alkylated diphenylamine such as nonylated diphenylamine of the formula



(D) The Fuel

The compositions of this invention, either (A) and (B) or (A), (B) and (C) can be added directly to fuels. 40 Preferably, however, they are diluted with the fuel to form an additive concentrate. These concentrates usually contain from about 10% to 80% by weight of the compositions of this invention and 20% to 90% by weight of the fuel.

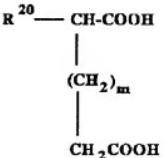
The fuel compositions of the present invention contain a major amount of a normally liquid fuel comprising  
45 (1) a hydrocarbonaceous petroleum distillate fuel such as motor gasoline as defined by ASTM specification D439 and diesel fuel or fuel oil as defined by ASTM Specification D396. Normally liquid fuel compositions comprising non-hydrocarbonaceous materials such as alcohols, ethers, organo-nitro compounds and the like (e.g., methanol, ethanol, diethyl ether, methyl ethyl ether, nitromethane) are also within the scope of this invention, and liquid fuels which are mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials are also contemplated. Examples of such mixtures are combinations of gasoline and ethanol and of diesel fuel and ether. Particularly preferred is gasoline, that is, a mixture of hydrocarbons having an ASTM distillation range from about 60°C at the 10% distillation point to about 205°C at the 90% distillation point.

Other fuels that can be employed are:

(2) Synthetic ester base oils that comprise the reaction of a monocarboxylic acid of the formula



55 or a dicarboxylic acid of the formula



5

10

with an alcohol of the formula



wherein  $\text{R}^{19}$  is a hydrocarbyl group containing from about 4 to about 24 carbon atoms,  $\text{R}^{20}$  is hydrogen or a hydrocarbyl group containing from about 4 to about 50 carbon atoms,  $\text{R}^{21}$  is a hydrocarbyl group containing from 1 to about 24 carbon atoms,  $m$  is an integer of from 0 to about 6 and  $n$  is an integer of from 1 to about 6.

Useful monocarboxylic acids are the isomeric carboxylic acids of pentanoic, hexanoic, octanoic, nonanoic, decanoic, undecanoic and dodecanoic acids. When  $\text{R}^{37}$  is hydrogen, useful dicarboxylic acids are succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid and adipic acid. When  $\text{R}^{37}$  is a hydrocarbyl group containing from 4 to about 50 carbon atoms, the useful dicarboxylic acids are alkyl succinic acids and alkaryl succinic acids. Alcohols that may be employed are methyl alcohol, ethyl alcohol, butyl alcohol, the isomeric pentyl alcohols, the isomeric hexyl alcohols, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, pentaerythritol, dipentaerythritol, trimethylolpropane, bis-trimethylolpropane, etc. Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyphthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles tetraethylene glycol and two moles of 2-ethylhexanoic acid, the ester formed by reacting one mole of adipic acid with 2 moles of a 9 carbon alcohol derived from the oxo process of a 1-butene dimer and the like.

A non-exhaustive list of companies that produce synthetic esters and their trade names are BASF as Gisosofluid, Ciba-Gelyg as Reolube, JCI as Emkarote, Oleofina as Radialube and the Emery Group of Henkel Corporation as Emery 2964, 2911, 2960, 2976, 2935, 2971, 2930 and 2957.

(3) The mineral oils having utility are mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Also useful are petroleum distillates such as VM&P naphtha and Stoddard solvent. Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers, chlorinated polybutylenes, etc.); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polypHENyls (e.g., biphenyls, terphenyls, alkylated polypHENyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

Unrefined, refined and rerefined oils, (as well as mixtures of two or more of any of these) can also be used in the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

(4) Polyalpha olefins such as alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of fuels that can be used. These are exemplified by oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxoalkylene polymers (e.g., methyl/polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about

1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters, or the C<sub>12</sub> Oxo acid diester of tetraethyleneglycol.

(5) Vegetable oils having utility as a fuel in this invention are those vegetable oils obtained without genetic modification, i.e., their monounsaturation content (as oleic acid) is below 60 percent. Vegetable oils having utility are canola oil, peanut oil, palm oil, corn oil, soybean oil, sunflower oil, cottonseed oil, safflower oil and coconut oil.

Generally, these fuel compositions contain an amount of the (A), (B) composition or (A), (B), (C) composition sufficient to improve one or more properties of the fuel such as rust-inhibition, dispersancy, etc., usually this amount is about 0.005 to about 0.5% by volume, preferably about 0.01 to about 0.1% by volume, based on the volume of such fuel compositions.

The fuel compositions can contain, in addition to the (A), (B) composition or (A), (B), (C) composition other additives which are well known to those of skill in the art. These include antiknock agents such as tetralkyl lead compounds, lead scavengers such as haloalkanes (e.g., ethylene dichloride and ethylene dibromide), deposit preventers or modifiers such as triaryl phosphates, dyes, cetane improvers, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents.

The fuel additive compositions of this invention can be added directly to the fuel, or they can be diluted with a substantially inert, normally liquid organic diluent such as naphtha, benzene, toluene, xylene or a normally liquid fuel as described above, to form an additive concentrate. These concentrates generally contain from about 20% to about 90% by weight of the composition of this invention and may contain, in addition, one or more other conventional additives known in the art or described hereinabove.

The fuel additive compositions of this invention can be provided in concentrate form with less than the above-indicated levels of additives, and then be added directly to the fuel along with additional amounts of the compositions of this invention and other known additives, or be further diluted with additives prior to the addition to the fuel until the level of additives is at the desired level.

When the composition of this invention comprises components (A) and (B), the (A) : (B) weight ratio is generally from 90:10 to 99.5:0.5, preferably from 95:5 to 99.5:0.5 and most preferably from 98:2 to 99.5:0.5.

When the composition comprises components (A), (B) and (C), the following states the ranges of these components in parts by weight:

| Component | Generally | Preferred | Most Preferred |
|-----------|-----------|-----------|----------------|
| (A)       | 80-99     | 90-99     | 95-98          |
| (B)       | 0.1-20    | 0.1-10    | 0.5-5.0        |
| (C)       | 0.001-1   | 0.01-.5   | 0.01-0.1       |

When the composition comprises components (A) and (B) or (A), (B) and (C) with (D) the following states the ranges of these components in parts by weight:

| Component | Generally         | Preferred        | Most Preferred   |
|-----------|-------------------|------------------|------------------|
| (A)       | 10-90             | 20-90            | 20-50            |
| (B)       | 0.1-20            | 0.1-10           | 0.5-5            |
| (C)       | zero or 0.001-1.0 | zero or 0.01-0.5 | zero or 0.01-0.1 |
| (D)       | 10-90             | 20-90            | 20-50            |

50 The components of this invention are blended together according to the above ranges to effect solution. The following Tables I - V outline examples so as to provide those of ordinary skill in the art with a complete disclosure and description on how to make the composition of this invention and is not intended to limit the scope of what the inventor regards as his invention. All parts are by weight.

**TABLE I**

| EXAMPLE | (A)                                 | (B)                        | POUR POINT °C | FREEZE POINT °C |
|---------|-------------------------------------|----------------------------|---------------|-----------------|
| 5       | 1 100 parts Example A-13 (baseline) |                            | -12           | -13.6           |
|         | 2 98.33 parts Example A-13          | 1.67 parts Example B-8     | -39           | -39.4           |
| 10      | 3 99.5 parts Example A-13           | 0.5 parts Acryloid 1267    | -39           | -40.7           |
|         | 4 99.0 parts Example A-13           | 1.0 part Acryloid 1267     | -39           | -40.6           |
| 15      | 5 98.0 parts Example A-13           | 2.0 parts Acryloid 1267    | -39           | -41.3           |
|         | 6 99.5 parts Example A-13           | 0.5 parts Viscoplex 10-930 | -39           | -41.3           |
| 20      | 7 99.0 parts Example A-13           | 1.0 part Viscoplex 10-930  | -42           | -42.5           |
|         | 8 98.0 parts Example A-13           | 2.0 parts Viscoplex 10-930 | -42           | -43.2           |

**TABLE II**

| EXAMPLE | (A)                                | (B)                      | POUR POINT °C | FREEZE POINT °C |
|---------|------------------------------------|--------------------------|---------------|-----------------|
| 30      | 1 100 parts Example A-2 (baseline) |                          | -3            | -5.8            |
|         | 2 99.5 parts Example A-2           | 0.5 parts Acryloid 1267  | -24           | -24.5           |
| 35      | 3 99.0 parts Example A-2           | 1.0 part Acryloid 1267   | -33           | -34.2           |
|         | 4 98.0 parts Example A-2           | 2.0 parts Acryloid 1267  | -33           | -34.6           |
| 40      | 5 99.5 parts Example A-2           | 0.5 parts Acryloid 1267  | -30           | -32.9           |
|         | 6 99.0 parts Example A-2           | 1 parts Viscoplex 10-930 | -30           | -32.5           |

50

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TABLE III

| EXAMPLE  | (A)                   | (B)                    | POUR POINT °C             | FREEZE POINT °C |
|----------|-----------------------|------------------------|---------------------------|-----------------|
| 5<br>15  | 100 parts Example A-1 |                        | -15                       | -16.8           |
|          | 2                     | 99.0 parts Example A-1 | 1.0 parts Acryloid 1267   | -36             |
| 10<br>20 | 3                     | 99.0 parts Example A-1 | 1.0 part Viscoplex 10-930 | -33             |
|          |                       |                        |                           | -35.0           |

TABLE VI

| EXAMPLE | (A)                      | (B)                        | POUR POINT °C | FREEZE POINT °C |
|---------|--------------------------|----------------------------|---------------|-----------------|
| 1       | 100 parts Example A-14   |                            | +3            | +1.1            |
| 2       | 98.75 parts Example A-14 | 1.25 parts Example B-8     | -12           | -13.4           |
| 3       | 99.5 parts Example A-14  | 0.5 parts Acryloid 1267    | -6            | -8.7            |
| 4       | 99.0 parts Example A-14  | 1.0 part Acryloid 1267     | -9            | -9.7            |
| 5       | 98.0 parts Example A-14  | 2.0 parts Acryloid 1267    | -9            | -10.9           |
| 6       | 99.5 parts Example A-14  | 0.5 parts Viscoplex 10-930 | -3            | -4.8            |
| 7       | 99.0 parts Example A-14  | 1.0 part Viscoplex 10-930  | -9            | -9.6            |

TABLE V

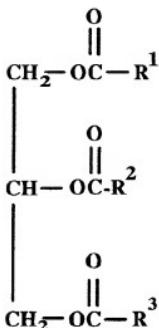
| EXAMPLE | (A)                      | (B)                     | POUR POINT °C | FREEZE POINT °C |
|---------|--------------------------|-------------------------|---------------|-----------------|
| 1       | 30 parts Example A-13    | 70 parts diesel fuel    | -12           | -13.8           |
| 2       | 29.85 parts Example A-13 | 69.65 parts diesel fuel | -30           | -31.4           |
| 3       | 29.85 parts Example A-13 | 69.65 parts diesel fuel | -27           | -29.1           |

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.

50

#### Claims

1. A composition, comprising:  
 55       (A) esters from the transesterification of at least one animal or vegetable oil triglyceride of the formula



with an alcohol  $R^4OH$  wherein  $R^1$ ,  $R^2$  and  $R^3$  are aliphatic groups containing from about 6 to about 24 carbon atoms and  $R^4$  is an aliphatic group containing from 1 to about 10 carbon atoms; and (B) a pour point depressant.

- 2 The composition of claim 1 wherein the vegetable oil triglyceride comprises sunflower oil, safflower oil, corn oil, soybean oil, rapeseed oil, meadowfoam oil or genetically modified sunflower oil, safflower oil, corn oil, soybean oil, rapeseed oil or meadowfoam oil.

3 The composition of claim 1 or claim 2 wherein the transesterification is carried out in the presence of a catalyst comprising alkali or alkaline earth metal alkoxides and at a temperature of ambient up to the decomposition temperature of any reactant or product.

4 The composition of any preceding claim wherein the pour point depressant is a mixed ester having low-temperature modifying properties of a carboxy-containing interpolymer, said interpolymer having a reduced specific viscosity of from about 0.05 to about 2 and being derived from at least two monomers, one of said monomers being a low molecular weight aliphatic olefin, styrene or a substituted styrene wherein the substituent is a hydrocarbyl group containing from 1 up to about 18 carbon atoms, and the other of said monomers being an alpha, beta-unsaturated aliphatic acid, anhydride or ester thereof, said ester being substantially free of titratable acidity and being characterized by the presence within its polymeric structure of at least one of each of three pendant polar groups which are derived from the carboxy groups of said ester:

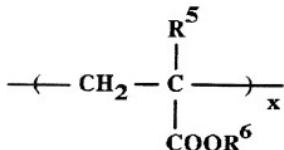
4 (A) a relatively high molecular weight carboxylic ester group, said carboxylic ester group having from 8 to 24 aliphatic carbon atoms in the ester radical,

4 (B) a relatively low molecular weight carboxylic ester group having from 3 to 7 aliphatic carbon atoms in the ester radical, wherein the molar ratio of (A):(B) is (1-20):1, and optionally

4 (C) a carbonyl-amino group derived from an amino compound having one primary or secondary amino group, wherein the molar ratio of (A):(B):(C) is (50-100):(5-50):(0.1-15).

5 The composition of claim 4 wherein the carboxy-containing interpolymer is a terpolymer of one molar proportion of styrene, one molar proportion of maleic anhydride, and less than about 0.3 molar proportion of a vinyl monomer.

6 The composition of any one of claims 1 to 3 wherein the pour point depressant is an acrylate polymer of the formula



10

wherein R<sup>5</sup> is hydrogen or a lower alkyl group containing from 1 to about 4 carbon atoms, R<sup>6</sup> is a mixture of alkyl groups containing from about 4 to about 24 carbon atoms, and x is an integer providing a weight average molecular weight (Mw) to the acrylate polymer of about 5000 to about 1,000,000.

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7. The composition of any one of claims 1 to 3 wherein the pour point depressant is a mixture of compounds having the general structural formula



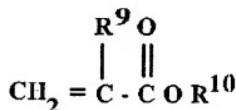
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wherein Ar, Ar' and Ar'' are independently an aromatic moiety containing 1 to 3 aromatic rings and the mixture includes compounds wherein moieties are present with 0 substituents, 1 substituent, 2 substituents and 3 substituents, R<sup>7</sup> and R<sup>8</sup> are independently an alkylene containing about 1 to 100 carbon atoms, and n is 0 to 1000.

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8. The composition of any one of claims 1 to 3 wherein the pour point depressant is a nitrogen containing polymethacrylate prepared by reacting a methacrylate ester of the formula

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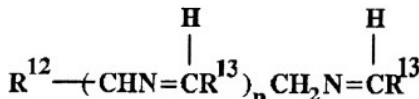
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wherein R<sup>9</sup> is hydrogen or an alkyl group containing from 1 to about 4 carbon atoms and R<sup>10</sup> is an alkyl group containing from 1 to about 24 carbon atoms, with a nitrogen-containing ester at from 0.1-20 moles of the nitrogen containing ester for each mole of the methacrylate ester.

40

9. The composition of any preceding claim further comprising an additive comprising  
 (1) a compound of the formula R<sup>11</sup>A wherein R<sup>11</sup> is an aliphatic group containing from about 6 to about 24 carbon atoms and A is -COOH and/or -OH or -NO<sub>2</sub>,  
 (2) a Schiff base of the formula

45



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- wherein R<sup>12</sup> is an aliphatic group containing from 1 to about 8 carbon atoms and R<sup>13</sup> is an aliphatic group containing from 1 to about 18 carbon atoms or an aromatic or substituted aromatic group containing from 6 to about 18 carbon atoms and n is 0 or 1;  
 (3) a carboxylic dispersant composition comprising the reaction product of a hydrocarbon substituted succinic acid-producing compound containing an average of at least about 12 aliphatic carbon atoms in the substituent and selected from succinic acids, anhydrides, esters and halides, with at least about one-half equivalent, per equivalent of acid producing compound, of an organic hydroxy compound or an amine containing at least one hydrogen attached to a nitrogen atom, or a mixture of said hydroxy

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compound and amine; and/or  
 (4) an antioxidant.

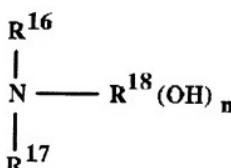
10. The composition of claim 9 wherein the amine reacted with the succinic acid producing compound has  
 5 the formula



wherein R<sup>14</sup> and R<sup>15</sup> are each independently hydrogen, or hydrocarbon, amino-substituted hydrocarbon, hydroxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, amino, carbamyl, thiocarbamyl, guanyl, and acylimidoyl groups provided that only one of R<sup>14</sup> and R<sup>15</sup> may be hydrogen.

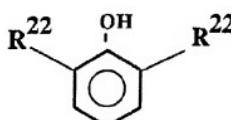
10. 11. The composition of claim 10 wherein R<sup>14</sup> is -C(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> and R<sup>15</sup> is hydrogen.

12. The composition of claim 9 wherein the organic hydroxy compound reacted with the succinic acid pro-  
 15 ducing compound has the formula

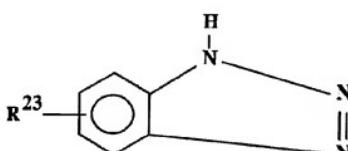


20 wherein R<sup>16</sup> and R<sup>17</sup> are aliphatic groups independently containing from 1 up to about 8 carbon atoms and R<sup>18</sup> is an alkylene group containing from 1 up to about 8 carbon atoms.

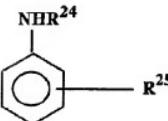
- 25 13. The composition of claim 9 wherein the antioxidant comprises  
 30 (a) at least one alkyl phenol of the formula



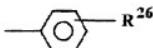
40 wherein R<sup>22</sup> is t-butyl;  
 (b) a benzotriazole of the formula



45 wherein R<sup>23</sup> is a methyl group; and/or  
 50 (c) at least one aromatic amine of the formula

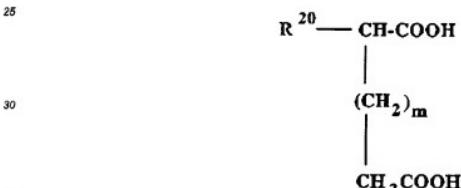


10 wherein R<sup>24</sup> is



and R<sup>25</sup> and R<sup>26</sup> are nonyl groups.

14. A fuel composition comprising a major amount of (D) a normally liquid fuel wherein the fuel comprises  
20 (1) a petroleum distillate;  
(2) a synthetic ester base oil comprising the reaction of a monocarboxylic acid of the formula  
 $R^{19}COOH$   
or a dicarboxylic acid of the formula



35 with an alcohol of the formula



- wherein R<sup>19</sup> is a hydrocarbyl group containing from about 4 to about 24 carbon atoms, R<sup>20</sup> is hydrogen or a hydrocarbyl group containing from about 4 to about 50 carbon atoms, R<sup>21</sup> is a hydrocarbyl group containing from 1 to about 24 carbon atoms, m is 0 or an integer of from 1 to about 6 and t is an integer of from 1 to about 6;  
(3) a mineral oil;  
(4) a polyalphaolefin; and/or  
(5) a vegetable oil;
- 45 and a minor amount of the composition according to any preceding claim.

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| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |                         |   |
|--|---|-------------------------|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim       | CLASSIFICATION OF THE APPLICATION (Int.CLS) |
| P,X  | WO-A-93 18115 (EXXON)<br>* the whole document *                               | 1,2,7                   | C10L1/02                                    |
| Y  | ---   | 3-6,<br>8-10,13,<br>14  | C10L1/14<br>C10L1/22<br>C10L1/18            |
| Y  | GB-A-2 099 449 (ERNER)<br>* the whole document *                              | 3,14                    |   |
| Y  | ---   |                         |   |
| Y  | WO-A-86 03221 (LUBRIZOL)<br>* page 52, line 9 - line 23 *                     | 4-6,9,<br>10,13,14      |   |
| X  | WO-A-92 11345 (HENKEL)<br>* the whole document *                              | 1,2                     |   |
| Y  | ---   | 6                       |   |
| Y  | EP-A-0 344 644 (ROHM)<br>* the whole document *                               | 6                       |   |
| Y  | US-A-4 161 392 (CUSANO ET AL.)<br>* the whole document *                      | 8                       |   |
| Y  | ---   |                         |   |
| Y  | WO-A-89 04845 (LUBRIZOL)<br>* the whole document *                            | 4,5,9,10                | TECHNICAL FIELDS<br>SEARCHED (Int.CLS)      |
| X  | ---   |                         | C10L  |
| Y  | GB-A-2 090 612 (I.F.P.)<br>* page 3, line 37 - line 45 *                      | 1,2,9<br>9,10,13,<br>14 |   |
| Y  | ---   |                         |   |
| Y  | EP-A-0 476 197 (ETHYL PETROLEUM ADD.)<br>* the whole document *               | 9,10,13,<br>14          |   |
| A  | FR-A-2 281 423 (MOBIL OIL)<br>* the whole document *                          | 11                      |   |
| A  | FR-A-2 354 346 (TEXACO)<br>* the whole document *                             | 12                      |   |
|  | ---   |                         |   |
|  | ---   |                         |   |
|  | ---   |                         |   |
| The present search report has been drawn up for all claims                       |   |                         |   |
| Place of search  | Date of completion of the search  | Examiner                |   |
| THE HAGUE  | 27 June 1994  | De La Morinerie, B      |   |
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| Category   | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int.Cl.) |
| P, X   | WO-A-94 10267 (EXXON)<br>* the whole document *                               | 1,2,9,14<br>-----  |   |
| The present search report has been drawn up for all claims                       |   |                    |   |
| Place of search  | Date of completion of the search  | Examiner           |   |
| THE HAGUE  | 27 June 1994  | De La Morinerie, B |   |
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